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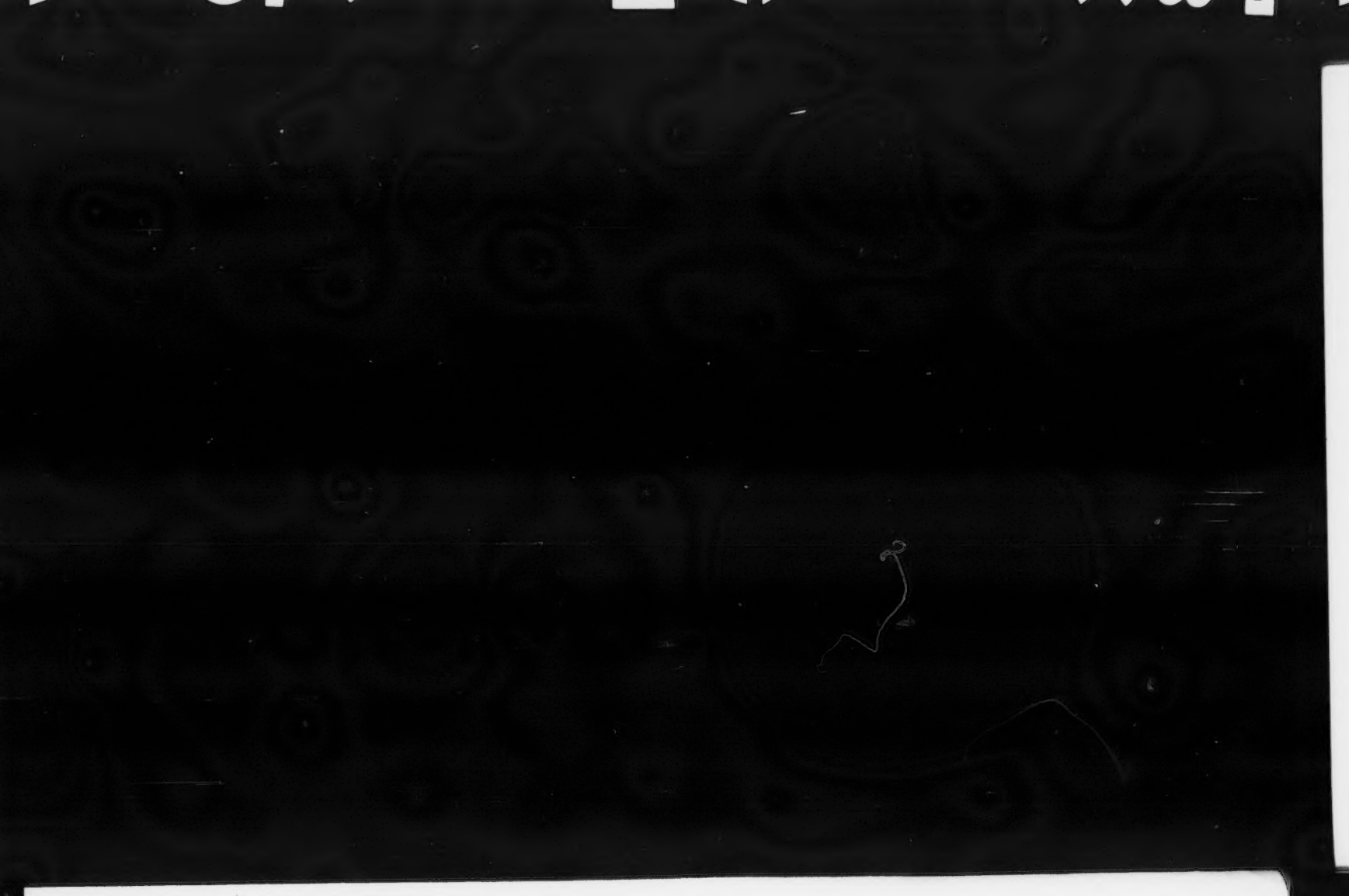

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VOL. 16, SEC. A. MAY, 1938 NUMBER 5

DENSITY DIFFERENCES AT THE CRITICAL POINT ACCORDING TO R. PLANK'S EQUATION OF STATE[1]

BY R. RUEDY[2]

Abstract

If R. Plank's equation of state is assumed to apply, the densities measured at two levels, 1 cm. apart, in a column of gas kept at the critical temperature, may differ by more than 5%. A large correction is therefore required for densities determined at the critical point unless the entire contents of the tube is vigorously stirred. Van der Waal's equation shows that the difference in level corresponding to a relative difference in density, $(\rho - \rho_c)/\rho_c$, is proportional to the third power of the relative difference; according to Wohl's equation it is proportional to the fourth, and according to Plank, to the fifth, power of the relative difference in density.

Introduction

The study of equations of state that apply alike to gases and to vapors reached its peak in the attempts to test van der Waal's equation, proposed in 1872, and to establish the range over which it applies. At the present time the success in separating isotopes opens the field to a renewed and more promising investigation with perfectly pure materials. Experiments for testing the equation of state of substances containing but one kind of molecule have not yet been undertaken, since only small volumes of such gases are available. The amount is nevertheless sufficient to permit a study of the behavior of gases at the critical point (3). The critical volume of heavy water is 2.74 cc. per gm. at a critical pressure, p_c, of 221.5 kg. per sq. cm. and a critical temperature, t_c, of 371.5° C., whereas the corresponding values for ordinary water are: $v_c = 3.066$ cc. per gm., $p_c = 225.5$ kg. per sq. cm., and $t_c = 374.23°$ C. (2).

The study of the critical point, or critical stage, as it might more properly be called, reduces in most cases to the determination of the critical temperature and the critical volume. The determination of the critical temperature is based on the disappearance of the meniscus between the liquid and its vapor, and the usual determination of the critical volume relies on the rule of the rectilinear diameter of the curve representing the densities of the liquid and the vapor as a function of the temperature.

The rule of the rectilinear diameter, enunciated by Cailletet and Mathias, states that when the density of the liquid and that of its saturated vapor are

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Contribution from the Division of Research Information, National Research Laboratories, Ottawa, Canada.

[2] *Research Investigator, National Research Laboratories, Ottawa.*

plotted as a function of the temperature, the average values of the two densities fall on a virtually straight line sloping in the direction of the higher temperatures. The density indicated by this line at the critical temperature is the critical density. Figs. 1 and 2 show the rectilinear diameter of krypton and xenon, water and carbon dioxide, according to the most recent measurements (6, 9). A remarkable feature of both curves is the rapid change in the densities of liquid and vapor as the critical region is approached; this almost sudden fall, or rise, to the common limit would alone justify the distinction of a critical point, where the slightest change in temperature produces a relatively large change in density. Recent, more accurate work seems to show that at low temperatures, instead of falling upon a perfectly straight line, the real average values lie slightly below the straight line, whilst near the critical stage the values lie above the middle line. The succession of average values represents a curve of the third degree with a pronounced point of inflection.

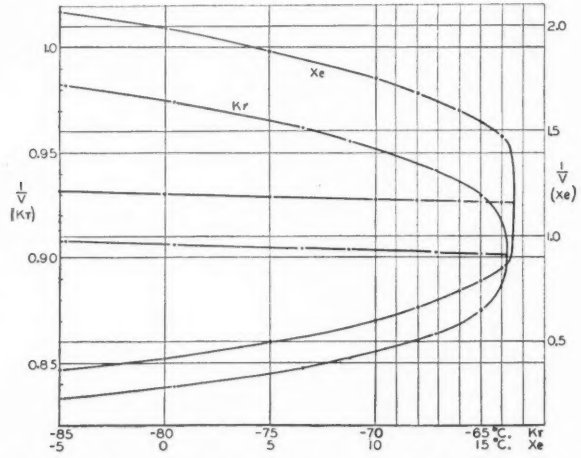

FIG. 1. *Density of krypton and xenon below the critical point as a function of the temperature.*

In the short method of determining the density at the critical stage a series of closed tubes filled to various heights with the liquid substance is used (1). When heat is applied to a tube in which the ratio between the mass of the substance and the inner volume of the tube is smaller than the critical density of the liquid, the meniscus falls, and the last traces of liquid are found to disappear at a definite temperature. At this temperature the computed average density is equal to the density of the saturated vapor. When the ratio between the mass and the volume is larger than the critical density and the tube is heated, the meniscus rises, and the last trace of the vapor disappears as a bubble at the top of the tube. At this stage the computed density of the contents must be equal to the density of the liquid boiling at constant volume

under the pressure of its own vapor. A series of these dew and boiling points is determined for various amounts of liquid in the tube, and the temperature is plotted as a function of the computed densities. At the critical temperature the rectilinear diameter intersects the curve at the critical density.

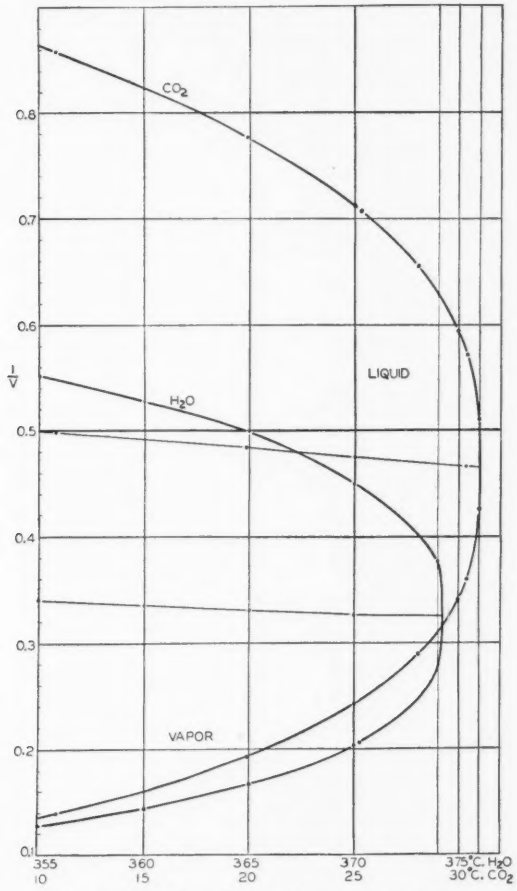

FIG. 2. *Density of carbon dioxide and water below the critical point as a function of the temperature (Michels, Eck).*

The critical temperature is deduced from the flat maximum of the curve obtained on plotting the temperature at which the meniscus disappears against the amount of liquid used.

Owing to the large changes in density caused by changes in temperature near the critical point, the meniscus always moves towards the top or the

bottom of the tube before disappearing, except in the quite unlikely case where the amount of substance present is such that the density is the true critical density. In practice the equilibrium is established so slowly in the range close to the critical point that when the temperature increases at a finite rate the system passes through the critical state before the boundary line between liquid and vapor has time to move. Even with slow heating, the influence of gravity causes the density in the tube to vary from level to level. The density differences to be expected on the basis of the equation of state at the critical point, and the corresponding changes in the optical and dielectric properties, are of interest for a better understanding of the behavior of liquid and vapor (8). A difficulty in this study is that the critical temperatures of only a few substances have been determined with a high degree of accuracy (ordinary water (2), 374.23° C.; krypton (6), −63.75° C. or 209.39° K.; carbon dioxide (7), −31.04° C.).

Equations of State of the Fifth Degree

The unequaled advantages of van der Waal's equation of state are its simple form and the wide range over which it gives a general explanation of the behavior of the properties of liquids and gases. It states that in place of the pressure $p = RT/v$ per unit area, computed for a gas with perfectly inert molecules, the pressure is for a real gas smaller by the amount a/v^2, because of the mutual attraction between molecules, which varies as a certain function of the distance, approximately as the inverse fourth power of the distance between molecules. More recent work suggests that the inverse sixth power would be more accurate. On the other hand the volume available for the free motion of the molecules is $(v - b)$ instead of v, owing to the finite size of the molecules; consequently,

$$p = \frac{RT}{v - b} - \frac{a}{v^2}.$$

The constants a and b are determined by the fact that at the critical stage the equation has a point of inflection at which the curve representing p as a function of v has three roots in common with the tangent. In reality the constant b also constitutes a correction for the repulsion between molecules at very close contact, forces which vary more nearly as the inverse twelfth power of the distance, and, therefore, affect the values at the highest pressure and smallest volumes. Wohl (13) takes them into account by adding the term $c/(v - b)^3$. The introduction of this term is justified also by the value of the ratio RT_c/p_cv_c obtained on the assumption that the curve representing p and v has at the critical point four points in common with the tangent; the ratio RT_c/p_cv_c is computed to be 3.75 instead of van der Waal's admittedly too small value of 2.67. The measured values for many organic compounds lie between 3.5 and 4.0, and no value as low as 3 is obtained for any gas. It would perhaps have been more correct to write the term that takes repulsion into account as c/v^4 or $c/(v - b)^4$ if the law of the inverse twelfth power is valid for the repulsive forces.

It is certain that the forces between molecules depend in a complicated way upon the distances between molecules, and upon the nature of the atomic forces, which vary from molecule to molecule. As long as the exact laws are but imperfectly known, the corrections to the pressure may be introduced by means of a series of terms according to descending powers of v or $(v - b)$, the number, n, of the terms depending on the accuracy desired and the numerical work thought to be justified. The difference between the molecular forces of different elements is considered by introducing so many constants that their number exceeds by at least one the number of terms in $(v - b)$ or v. R. Plank's recent equation can be used when five terms are involved (10):

$$p = \frac{RT}{(v - b)} - \frac{a_2}{(v - b)^2} + \frac{a_3}{(v - b)^3} - \frac{a_4}{(v - b)^4} + \frac{a_5}{(v - b)^5} .$$

On the assumption that at the critical stage the curve representing p as a function of v has five points in common with the tangent and that this tangent is parallel to the v-axis, the following relations are obtained:

$$\frac{RT_c}{p_c(v_c - b)} = n = 5$$

$$\frac{RT_c}{p_c v_c} = n(1 - b/v_c) = n(1 - 1/\alpha)$$

with $$b = v_c/\alpha = M/\alpha\rho_c .$$

$$a_2 = (n - 1)(\alpha - 1)bRT_c/2 = 2b(\alpha - 1)RT_c \text{ for } n = 5$$
$$a_3 = (n - 1)(n - 2)(\alpha - 1)^2b^2RT_c/1 . 2 . 3n = 2b^2(\alpha - 1)^2RT_c$$
$$a_4 = (\alpha - 1)^{n-2}b^{n-2}RT_c = b^3(\alpha - 1)^3RT_c$$
$$a_5 = (\alpha - 1)^{n-1}b^{n-1}RT_c = b^4(\alpha - 1)^4RT_c .$$

The constant $\alpha = v_c/b$ remains arbitrary and may be so chosen that RT_c/p_cv_c agrees with the measured values (Table I).

TABLE I

VALUES OF $\alpha = v_c/b$ AND OF RT_c/p_cv_c

RT_c/p_cv_c	α	Examples of values of RT_c/p_cv_c
3.33	3	Oxygen, 3.34; neon, 3.25
3.44	$3\frac{1}{2}$	Argon, nitrogen, 3.43; krypton, 3.44
3.57	$3\frac{1}{2}$	Xenon, 3.6
3.66	$3\frac{3}{4}$	Carbon dioxide, 3.636
3.75	4	Benzene, 3.71; pentane, 3.77
4	5	Propyl alcohol, 4

An equation of state of the fifth degree was proposed by van der Waal who put

$$b = b_o - b_1/v + b_2/v^2 .$$

Such an equation enters into modern theories of the liquid state (4, 10, 11). That the value of b is a constant over the whole range of temperatures is not to be expected, since the molecular spectrum reveals an increase in the distance between the atoms when the excitation is increased by heat, while at the same time the higher energy at the higher temperatures produces a greater deformation of the molecules and causes closer approach of their centres during collisions. To a certain extent the two effects cancel each other.

The equation of the fifth degree will apply alike to liquids and gases only if there is no shift in the importance of the terms in $(v - b)$ during the transition from the liquid to the gaseous state. Such a shift, which is caused by a change in the laws of attraction and repulsion, might be expected when the molecules acquire or lose a certain amount of the orientation that exists in the solid state, often as the result of ionization (salts). There is of course no complete separation between liquid and solid state and, therefore, no sharp gap that would mark presence or absence of orientation, no more than there is, as regards viscosity, a sharp boundary between liquid and solid state. Glass as an undercooled liquid, and liquid crystals, in which patches of oriented molecules are merely due to the unusual length of the molecules, illustrate how the different states of matter shade one into the other. But any possible orientation in the liquefied noble gases, such as neon and argon, does not involve the functioning of forces not already present in the gas. The properties of solid neon and argon seem to be governed by exactly the same forces that cause the gases to deviate from the ideal law (5); consequently, there exists a certain continuity of the gaseous, the liquid, and even the solid states of neon and argon. The facts that throughout a wide range of corresponding temperatures, from the lowest to at least three-fourths of the critical temperature, the density of liquid xenon is equal to that of liquid oxygen, and that the densities of their vapors are also the same, despite the difference in their chemical properties, suggest that the effect of the orientation of oxygen molecules need not be included as a new and important factor in the equation of state.

The Barometric Formula According to R. Plank's Equation

When volumes are replaced by densities, Plank's equation may be written

$$p = RT\frac{\rho}{(M - b\rho)} - a_2\frac{\rho^2}{(M - b\rho)^2} + a_3\frac{\rho^3}{(M - b\rho)^3} - a_4\frac{\rho_4}{(M - b\rho)^4} + a_5\frac{\rho^5}{(M - b\rho)^5}.$$

If the pressure at any point in the gas is due to the column of gas above it, then

$$dp = -\frac{\rho}{1033}dh,$$

the height being expressed in centimetres and the pressure in atmospheres; consequently,

$$-\frac{dh}{1033d\rho} = RT\frac{M}{(M-b\rho)^2} + \sum_{r=2}^{r=5}(-1)^{r+1}rM\frac{\rho^{r-2}}{(M-b\rho)^{r+1}}.$$

If $1/\alpha\rho_c$ is written in place of b/M, an integration gives for the height h, where the density is ρ,

$$\begin{aligned}\frac{h}{1033} = {} & RTln\frac{M}{\rho}(1-\rho/\alpha\rho_c) - \frac{RT}{M}(1-\rho/\alpha\rho_c)^{-1} \\ & + \frac{RT_c}{2M}(\alpha^4-1)(1-\rho/\alpha\rho_c)^{-2} \\ & - \frac{RT_c}{3M}(1+2\alpha+3\alpha^2)(\alpha-1)^2(1-\rho/\alpha\rho_c)^{-3} \\ & + \frac{RT_c}{4M}(1+3\alpha)(\alpha-1)^3(1-\rho/\alpha\rho_c)^{-4} \\ & - \frac{RT_c}{5M}(\alpha-1)^4(1-\rho/\alpha\rho_c)^{-5},\end{aligned}$$

apart from an arbitrary constant. On introducing

$$1-\frac{\rho}{\alpha\rho_c} = \frac{\alpha-1}{\alpha}\left(1-\frac{\rho_c-\rho}{(\alpha-1)\rho_c}\right) = \frac{\alpha-1}{\alpha}\left(1-\frac{y}{\alpha-1}\right)$$

this formula becomes

$$\begin{aligned}\frac{h}{1033} = {} & \frac{RT}{M}\left(ln\frac{\alpha-1}{\alpha}\frac{M}{\rho_c} + ln\left(1-\frac{y}{\alpha-1}\right) - ln\left(1+y\right) - \frac{\alpha}{\alpha-1}\left(1-\frac{y}{\alpha-1}\right)^{-1}\right) \\ & + \frac{\alpha}{\alpha-1}\frac{RT_c}{M}\left(\frac{\alpha}{2}\left(1+\alpha+\alpha^2+\alpha^3\right)\left(1-\frac{y}{\alpha-1}\right)^{-2}\right. \\ & -\frac{\alpha^2}{3}\left(1+2\alpha+3\alpha^2\right)\left(1-\frac{y}{\alpha-1}\right)^{-3} + \frac{\alpha^3}{4}\left(1+3\alpha\right)\left(1-\frac{y}{\alpha-1}\right)^{-4} \\ & \left. - \frac{\alpha^4}{5}\left(1-\frac{y}{\alpha-1}\right)^{-5}\right).\end{aligned}$$

When the column of gas is at the critical temperature, T_c, the difference in height, Δh, between the layer where the density is ρ and that where the density is ρ_c, or where $y = (\rho - \rho_c)/\rho_c = 0$, is given by

$$\frac{M}{RT_c}\frac{\Delta h}{1033} = ln\left(1 - \frac{y}{\alpha - 1}\right) - ln\left(1 + y\right) - \frac{\alpha}{\alpha - 1}\left(1 - \frac{y}{\alpha - 1}\right)^{-1}$$

$$+ \frac{\alpha}{\alpha - 1}\left(\left(1 + \alpha + \alpha^2 + \alpha^3\right)\left(1 - \frac{y}{\alpha - 1}\right)^{-2}\right.$$

$$+ \frac{\alpha^2}{3}\left(1 + 2\alpha + 3\alpha^2\right)\left(1 - \frac{y}{\alpha - 1}\right)^{-3}$$

$$\left. + \frac{\alpha^3}{4}\left(1 + 3\alpha\right)\left(1 - \frac{y}{\alpha - 1}\right)^{-4} + \frac{\alpha^4}{5}\left(1 - \frac{y}{\alpha - 1}\right)^{-5}\right).$$

For short columns, y is small, not more than 5%, and after development of the powers of $(1 - y/(\alpha - 1))$ in series the expression can be reduced, in practice, to

$$\frac{\Delta h}{1033} = -\frac{\alpha^6}{(\alpha - 1)^6}\frac{RT_c}{M}\left(\frac{y^5}{5} - \frac{(\alpha - 7)}{6(\alpha - 1)}y^6\right).$$

This expression gives the difference in height above or below the level where the density is ρ_c and that where the relative density difference is y. For all substances, the height depends in the same way on the relative density difference y and on the value of $\alpha = v_c/b$. Thus with $R = 82.1$

$$\frac{M}{T_c}\Delta h = 9.66 \times 10^5\left(\frac{y^5}{5} + \frac{y^6}{3}\right), \quad \text{for} \quad \alpha = 3,$$

$$\frac{M}{T_c}\Delta h = 4.76 \times 10^5\left(\frac{y^5}{5} + \frac{y^6}{6}\right), \quad \text{for} \quad \alpha = 4,$$

$$\frac{M}{T_c}\Delta h = 3.23 \times 10^5\left(\frac{y^5}{5} + \frac{y^6}{12}\right), \quad \text{for} \quad \alpha = 5.$$

Apart from the ratio α, the nature of the gas enters into the factor M/T_c, which varies from 0.1 to 0.5 and higher.

The heights measured from the level with the critical density in question and computed by using various equations of state (11), are compared in Table II. For Plank's equation only the values for $\alpha = 3$ and $\alpha = 4$ are given; the heights for $\alpha = 5$ are a third of those obtained for $\alpha = 3$, and indicate therefore an even more pronounced variation in density with the height. When the column of gas is at the temperature $T = T_c(1 + t/T_c)$, the difference in height between the layer at which the density is ρ, and that

at which it is ρ_c, is equal to the height Δh_c computed for the critical temperature plus a correction such that

$$\frac{\Delta h}{1033} = \frac{\Delta h_c}{1033} + \frac{R}{M}\frac{t}{T_c}\left(ln \frac{1 - \frac{y}{\alpha - 1}}{1 + y} - \alpha \frac{y}{1 - \frac{y}{\alpha - 1}} \right).$$

Although Plank's equation has been applied to but a few substances, carbon dioxide and water among them, there is no doubt that with van der Waal's equation the contact between the p,v curve and the horizontal tangent at the critical point is not sharp enough to give agreement with the measured values.

TABLE II

DENSITY CHANGES IN A COLUMN OF GAS OF MOLECULAR WEIGHT M NEAR THE CRITICAL TEMPERATURE, T_c

Percentage change y	$\frac{M}{T_c}\Delta h$, cm.			
	van der Waal	A. Wohl	R. Plank	
			$\alpha = 3$	$\alpha = 4$
−0.5	0.006			
−1	0.05	0.0003		
−2	0.4	0.0044	0.0006	0.0003
−3	1.3	0.024	0.0046	0.0023
−4	3.2	0.078	0.019	0.010
−5	6.2	0.185	0.058	0.029
−6	10.7	0.389	0.141	0.070

On the Experimental Determination of the Density at the Critical Stage

The direct method of determining the density differences in a column of gas near the critical temperature by means of small floats of varying buoyancy is cumbersome, and is inaccurate when the density varies rapidly with the height. The use of floats suspended from a fine quartz spiral prevents stirring of the entire contents, and requires that corrections be applied for the suspension system when the float and a portion of the spring dip into the liquid. A closely wound spiral offers a considerable resistance to the passage of the material from the space enclosed by the spiral to the space between the spiral and the walls of the tube, or vice versa. Grids of thin wires from 0.5 to 3 mm. in diameter, spaced 2 to 20 mm. apart, are actually used as shields against strong air currents. Stirring of the contents of the tube outside the spiral is not likely to affect the material held inside the spiral since the gas between the wires is virtually at rest, and since the pressure differences near the critical point are much smaller than the forces causing

a strong air current. The density may vary without an appreciable change in pressure, whereas, on the contrary, a change in temperature in the critical region produces a much larger variation in density than at any other temperature. Thorough mixing in a reasonable time is obtained, therefore, only by heating the contents of the tube, and densities read while the temperature is decreasing are likely to be lower than the values found when the temperature is increasing.

The optical methods used for obtaining the density differences are disadvantageous owing to the turbidity of the fluid at the critical point. The method developed by Töpler for studying streaks which depends directly upon the existence of a density gradient in the material, seems nevertheless to suit the purpose. In this method the column of gas is placed between a projecting lens and an evenly illuminated surface that serves as a bright background. The lens projects on a screen an image of the background, and by cutting off from one side all the rays of light but those in the very axis of the optical system each point on the screen is made to correspond to a point in the background. Hence any deflection of the ray that might be caused by a region of varying density between background and lens causes the image point to lose brightness in favor of the region of uniform density. The sensitivity of the method is greater, the narrower the space between the optical axis and the edge limiting the pencil of rays, and the greater the distance s between the lens and the edge used for reducing the cross section of the pencil of light. The distance s may amount to a few metres, and the distance e from edge to axis to a few microns. Experience shows that when an arc lamp is used a deflection corresponding to about one-eighth second, or about 0.6×10^{-6} radian, may be detected by this means.

In a column of gas, in which the density varies with the height, a beam of light arriving in a virtually horizontal direction is bent into arcs of radius

$$R = \frac{n}{\text{grad } n} = \frac{d}{e} ,$$

where d is the length of the path in the layer considered, and e is the small angle that the emerging ray forms with the incident ray. In the general case, n and grad n vary slowly, and the values of R are so large that the path described is a single flat arc, or a straight line. For gases and vapors

$$n = 1 + c\rho/\rho_o \; ; \quad \text{grad } n = \frac{c}{\rho_o} \text{grad } \rho ,$$

where ρ_o is the density at 0° C. and 760 mm. of mercury, and c is a small constant, equal to 0.000296 in the case of nitrogen ($\rho_o = 0.00125$, $\rho_c = 0.32$), 0.000335 for carbon dioxide ($\rho_o = 0.002$, $\rho_c = 0.46$), 0.000067 for neon ($\rho_o = 0.0009$, $\rho_c = 0.484$), 0.000428 for krypton ($\rho_o = 0.0058$, $\rho_c = 0.9085$). The value of n is not likely to exceed 1.1 at the critical stage; consequently, in practice,

$$e = \frac{d}{n} \text{ grad } n = \frac{cd}{\rho_o} \text{grad } \rho .$$

When the average change of ρ over a distance of 1 cm. is about 5%, and the light traverses a column of gas 1 cm. thick in the section containing the axis of the tube, the angle of deflection e is at least 10^{-5}, and Töpler's method for detecting streaks should reveal at a glance the density differences in a column of gas kept at a temperature close to the critical.

In substances possessing strong molecular absorption bands in the near infra-red, such as the OH band, the position of the band may undergo a strong shift as the liquid or vapor approaches the critical point. The influence of the approach to a common limit upon the refractive index in the visible spectrum remains to be investigated.

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The articles in the van der Waal's Centenary number of Physica were received too late to be of use for the present paper.

A DEVICE FOR THE AUTOMATIC REGULATION OF THE CURRENT IN A SHEARER X-RAY TUBE[1]

By Hugh Le Caine[2]

Abstract

A device for rendering automatic the operation of a Shearer X-ray tube is described. Its functions are: (i) to regulate the leak valve mechanically so as to maintain a constant current; (ii) to disconnect the high tension transformer and close the leak valve when a failure of any part of the vacuum system causes high pressure and excessive tube current, the tube restarting as soon as the pressure again becomes low enough.

Standard, inexpensive, radio parts, a small motor, and suitable gearing to connect motor and valve are all that are required. The limits within which the tube current can be held may be made very narrow.

In a Shearer X-ray tube, the current is regulated by adjustment of the amount of air which flows through a needle or leak valve into the tube. It is impossible to keep the tube current fixed over long periods without adjustment of the valve. The device described below has been used to make these adjustments automatic. Its action may be seen by reference to the circuit diagram. The tube current flowing through R_1 and R_2 produces a voltage drop, which, together with a fixed voltage B_1, is applied to the grid of the tube T_1. T_1 is operated close to the "cut-off point." In this region the curvature of the tube's characteristic surface is such that the "dynamic plate resistance", $\frac{\partial E_p}{\partial I_p}$, may be considered a function of the grid voltage. In this way the grid controls the fraction of the alternating voltage, E_1, which appears across the plate resistor R_4. In the grid circuit of the thyratrons, T_2 and T_3, this variable fraction of E_1 is combined with a second alternating voltage E_2 of the same frequency as E_1 and 180° out of phase with it. The magnitudes of E_1 and E_2 are so chosen that for a definite potential applied to the grid of T_1 the resultant alternating voltage in the grid circuit of T_2 and T_3 is zero. Above and below this critical potential, the resultant voltage has opposite phases. It may be seen from the diagram that the plates of T_2 and T_3 are at alternating voltages in phase with E_1 and E_2 respectively. With the bias battery, B_2, correctly adjusted, a resultant alternating voltage in the grid circuit of T_2 and T_3 may be made to fire either T_2 or T_3, depending upon its phase. A corresponding field of the motor is energized, and the motor turns in one direction or the other. If R_1 and B_1 are so adjusted that the desired X-ray tube current places the grid of T_1 at the critical potential mentioned, any change in tube current will cause the motor to turn. This motion may be transmitted to the valve through suitable gearing; thus the leak may be increased or decreased until the desired value of tube current is re-established.

[1] *Manuscript received March 14, 1938.*

Contribution from the Department of Physics, Queen's University, Kingston, Ontario, Canada.

[2] *Physics Student, Queen's University.*

To reduce the wear on the mechanism, the range of current values over which the thyratrons remain non-conducting should be made as wide as experimental conditions permit. The width of the range may be controlled by varying the thyratron bias. If R_1 is changed to maintain a different tube current, the relative sensitivity remains the same.

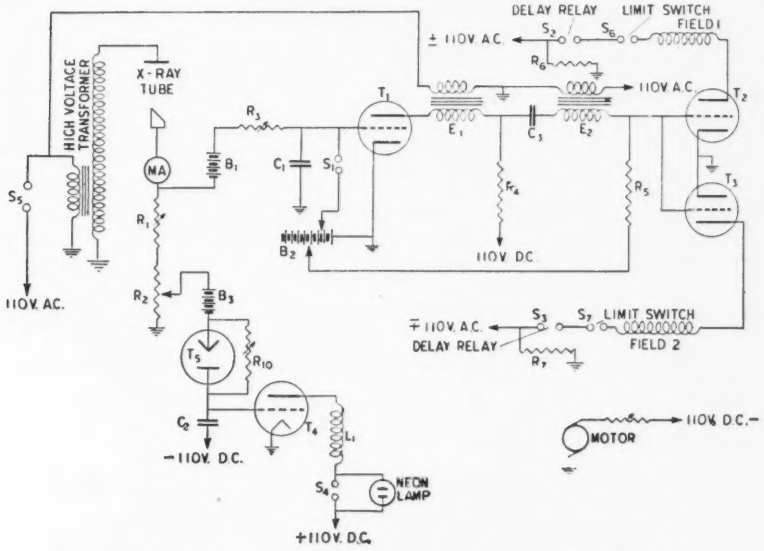

FIG. 1. *Device for regulating the current in a Shearer X-ray tube.*

B_1, *90 v.*
B_2, *18 v., 1½ v. taps provided.*
B_3, *45 v.*
R_1, R_2, *determined by X-ray tube current.*
R_3C_1, *approx. 10 sec.*
$R_{10}C_2$, *approx. 200 sec.*
R_4,R_5, *approx. 20,000 ohms.*
C_3, *2 μf*
E_1, *approx. 40 v. R.M.S.*
E_2, *approx. 10 v. R.M.S.*
L_1S_5, *circuit-closing relay.*
T_4, *power triode;* T_5, *diode.*
Neutrals of a-c. and d-c. supply grounded.

Overshooting must be avoided by allowing time for the pressure to become uniform over the vacuum system after an adjustment of the valve. A contact, S_1, on the motor, stops it after every revolution by bringing the grid momentarily to the proper potential. The grid circuit is then allowed to charge through R_3 to the difference in potential between B_1 and the tube current drop across R_1 and R_2. If the voltage necessary to cause firing of the thyratrons is E volts below the normal bias, the time, t, between revolutions of the motor can be expressed as a function of e, the resultant alternating voltage in the grid circuit.

$$t = C_1R_3 \log (1 - e/E) .$$

Thus, the rate at which the valve is adjusted becomes smaller as the operating value of current is reached, and is zero when $e = E$. The edge of the operating

range is approached asymptotically. Owing to random fluctuations in the tube current its mean value will be at the centre of the range. The factor C_1R_3 is the time constant of the grid circuit (neglecting $R_2 + R_1$), and can be adjusted to give the most rapid correction possible without overshooting. If desired, the speeds of increasing and decreasing the leak may be made unequal by shifting the potential on the battery side of S_1 from the centre of the operating range.

The contact at S_1 must be closed for a small part of the revolution, and must be made in such a way that the motor cannot stop with the contact closed. A small spring may be provided to rotate the armature past this point. An alternative scheme which positively avoids "dead spots" is to connect a double-pole, double-throw relay so that the circuit is closed only while the armature is between the energized and the non-energized positions. The latter method was used, as such a relay was available.

It is important that the tube T_1 be correctly chosen and operated on a suitable part of its characteristic surface. If ΔI is the greatest deviation of X-ray tube current from operating value which can occur without turning the motor, $I/\Delta I$ may be called the relative sensitivity of the device. It may be expressed as a function of ΔE_T, the excess of bias applied to the thyratrons over the firing point bias, according to the equation

$$\frac{I}{\Delta I} = E_{B_1} \frac{\partial E_{R_5}}{\partial E_g} \frac{1}{\Delta E_T},$$

where E_{B_1} is the voltage of the battery B_1, E_{R_5} is the alternating voltage developed in R_5, E_g is the potential of the grid of T_1. Firing is assumed to occur when the peak value of the resultant alternating voltage exceeds ΔE_T.

If operation is confined to a portion of the tube's characteristic surface where $\frac{\partial^2 E_p}{\partial I_p^2} = 0$, and it is assumed that the area of this region is not zero, then,

$$\frac{\partial E_{R_5}}{\partial E_g} = \frac{E_1 \dfrac{\partial^2 E_p}{\partial E_g \, \partial I_p} R_b}{\left(\dfrac{\partial E_p}{\partial I_p} + R_b\right)^2}.$$

R_b is the a-c. plate load, approximately R_4 and R_5 in parallel. To obtain the greatest sensitivity, the tube should be so chosen that $\frac{\partial E_{R_5}}{\partial E_g}$ is as great as possible. R_b is limited by the maximum resistance which may be introduced into the grid circuit of the thyratrons. Pentodes have very large values of $\frac{\partial^2 E_p}{\partial E_g \, \partial I_p}$, but are less suitable in other respects than triodes of the medium μ class. Types '27, '01A, or 6C5, operating on the negative side of the projected cut-off point, are satisfactory, although the condition $\frac{\partial^2 E_p}{\partial I_p^2} = 0$ is satisfied over a rather small range. The above expression for sensitivity,

$I/\Delta I$, has been verified experimentally, a '27 tube being used for T_1. The circuit will maintain its calibration during the life of T_1. When the tube is operated properly, the dynamic plate resistance is independent of plate voltage and heater voltage. Thus the circuit is not affected by changes in supply voltages. Owing to the use made of T_1, changes in the characteristics of the thyratrons do not cause a shifting of the value of current to be maintained, and affect only the sensitivity.

If the motor is connected as shown, it must be provided with a split field. This type of motor is now commercially available. Any thyratron capable of controlling sufficient power is satisfactory. Type 885, the least expensive thyratron, will control 20 watts, when the external impedance is suitably chosen. Type FG-17 was used, as it was available. Variations of the circuit will readily occur to those interested in the design. Between motor and valve, gearing from a discarded clock forms a convenient connection, providing a large number of ratios. Springs should be used to reduce the lost motion to a point at which the motor will pick up the valve in at least one revolution. A fine, closely wound helix of steel wire, about No. 28, is a very satisfactory belt. Limit switches, S_6, S_7, normally closed, are placed in the field circuit to limit the travel of the valve.

The thermal delay relays (S_2, S_3, R_6, R_7) are not required unless the a-c. supply is disconnected frequently, but are a convenience in any thyratron circuit. They can be made cheaply from a "blinker plug", or thermal interrupter. This is stripped down to the fibre disc supporting the compound bar and contacts, and the heating coil (R_6, R_7) is connected as shown. The time taken for the contacts to close may be adjusted by bending the fixed contact leaf.

Occasionally the pressure in the X-ray tube rises temporarily, owing to a failure of the power supply to the pump, or for other reasons. The tube current may then become too great. Overload protection which removes the voltage from the high tension transformer primary is therefore provided. The circuit then remains open for a period depending on the severity of the overload. The tube current drop through a part of R_2 is applied to the grid of a power tube T_4 through a bias battery B_3 and rectifier T_5. When the resultant grid potential drops to a certain value, the relay opens the transformer primary circuit. The time constant involved in the opening action is small. The rectifier allows the grid to charge positively only through the shunt path R_{10}. The time constant, $R_{10}C_2$, is quite large. The duration of a severe load is approximately the opening time of the relay. The charge acquired by the grid condenser, and therefore the time for which the circuit is open, is proportional to the extent of the overload. Since E_1 is obtained from a transformer connected across the high tension transformer primary, the valve closes automatically at full speed whenever the tube is shut down. It was intended originally to provide for a limited number of automatic reclosures. This has been found unnecessary, since the rapidity of release of the circuit prevents any harm during the severest overload possible. This action allows the tube to restart as soon as conditions permit.

The cathode of T_5 should be heated from the d-c. line. Then a power interruption which causes the cathode to cool also allows C_2 to charge negatively; this prevents the relay L_1S_5 from closing before the circuit is operative.

None of the circuit constants are critical. R_1, R_2 should be wire wound; R_3, R_{10} may be carbon. R_1, R_3, R_{10} are more conveniently adjusted if suitably tapered. B_1 and B_3 may be replaced by separate power packs; B_1 must be stabilized by a 90 volt neon lamp in the conventional manner. B_3 may be replaced by a low resistance potentiometer between ground and -110 d.c. The highest permissible resistance is determined by the time during which the contact is closed. The neon lamp is required to absorb surges when a quick opening relay is used.

The device has been used for making long exposures and has operated without attention for periods of 200 hr. at a time. The same arrangement could be used for mechanically regulating any device for controlling a quantity having associated with it a continuously changing potential. The impedance of the circuit could be high. The circuit is not suited for use with low potentials such as those found in ordinary bridge circuits.

Acknowledgment

The writer wishes to thank Dr. J. A. Gray for the use of his laboratory.

NOTE ON "THE ALTITUDE EFFECT ON THE SPECIFIC IONIZING POWER AND ZENITH ANGLE DISTRIBUTION OF COSMIC RAYS", BY DAROL K. FROMAN AND J. C. STEARNS

Dr. M. L. Rowles, Macdonald College, has kindly pointed out to the writers two errors in the paper of the above title appearing in the Canadian Journal of Research, A, 16 : 29-40. 1938.

On p. 33, the last line should read: $\frac{\pi r \tan \alpha}{4}$.

On p. 34, Equation (7) should read: $d = d_1 + 2s$.

A correction for the first error increases the values quoted for J_o, N_1 and N_2, and decreases the value quoted for i, by 7%. In the original paper the calculations were made with Equation (7) in its correct form.

D. K. Froman.

Macdonald College,
Macdonald College P.O., Que.
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THE ALKALOIDS OF FUMARIACEOUS PLANTS

XVII. *CORYDALIS CASEANA* A. GRAY[1]

BY RICHARD H. F. MANSKE[2] AND M. R. MILLER[3]

Abstract

A chemical examination of *Corydalis caseana* has yielded a total of ten alkaloids. Of these, protopine, α-allocryptopine, bicuculline, corypalmine, and scoulerine are known alkaloids. The remaining five appear to be new and include: *caseanine*, $C_{21}H_{25}O_4N$; *casealutine* and *alkaloid F34*, isomeric and represented by $C_{20}H_{23}O_4N$; *alkaloid F33*, $C_{19}H_{21}O_4N$; and *alkaloid F35*, $C_{20}H_{23}O_4N$. The new alkaloids are phenolic except caseanine which is the monomethyl ether of casealutine and the dimethyl ether of aurotensine.

Corydalis caseana A. Gray, a species native to high moist canyons of the Plumas National Forest, California, has been subjected to a preliminary examination by one of the present authors (4). Owing to the pressure of other duties its further investigation was temporarily suspended. More material was however collected, and some of the fractions were examined in the National Research Laboratories, Ottawa, Canada. The present joint communication is thus the result of the collaborative undertaking.

Of the ten alkaloids thus far isolated, only five, namely, protopine, α-allocryptopine, bicuculline, corypalmine, and scoulerine have been previously encountered, and with the exception of corypalmine are all present in *C. scouleri* (2). The remaining five alkaloids, though by no means conclusively characterized, appear to be new. Of these, *caseanine* (F36) is the most abundant. Its probable empirical formula, $C_{21}H_{25}O_4N$, containing four methoxyl groups, is identical with that of tetrahydropalmatine, of glaucine, and of methylpavine (5). Its possible identity with an optically active form of the last is under consideration. Incidentally, it is the dimethyl ether of aurotensine (3). The remaining four alkaloids, F32, F33, F34, and F35, which were present in small amounts only, are all phenolic. For their further examination more material will be required, although one of them, F32, has been encountered in another species, *C. lutea*, now under investigation. On methylation it yields caseanine, and since it contains only one hydroxyl group it is one of the four possible O-desmethyl derivatives of caseanine. The term *casealutine*, derived from the specific names of its two botanical sources, is proposed for this alkaloid.

[1] *Manuscript received January 25, 1938.*
Contribution from the Division of Chemistry, National Research Laboratories, Ottawa, Canada, and the Agricultural Experiment Station, University of Nevada, Reno, Nevada, U.S.A.
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[3] *Research Chemist, Agricultural Experiment Station, University of Nevada.*

Experimental

The procedure developed by one of us (1) was used to effect a separation into the various fractions. In the following summary the numbering of the alkaloids is sequential to that recently recorded (3). There was available a total of 5.5 kg. of dried plant material.

Base hydrochlorides extracted from aqueous solution by means of chloroform—

BC—Non-phenolic bases,—Caseanine (F36), Bicuculline.
BCE and EEC—Phenolic bases precipitated by carbon dioxide,—*l*-corypalmine, F32, F33, F34, F35.

Base hydrochlorides not extracted from aqueous solution by means of chloroform—

BS—Non-phenolic bases,—Protopine, α-Allocryptopine.
BSE and EES—Phenolic bases precipitated by carbon dioxide,—Scoulerine, F33.

Bicuculline

The fraction (BC), which had been thoroughly washed with water and dried, was dissolved in hot methanol. The base, which rapidly separated in crystalline form, was filtered off. It melted at 195° C.* Admixture with a specimen of bicuculline melting at 196° C. caused no depression in the melting point. It was further characterized by conversion to the low melting form (m.p. 177° C.) which proved to be identical with an authentic specimen. The yield was 0.20%.

Caseanine (F36)

The methanolic filtrate from the bicuculline was boiled with charcoal, filtered, and evaporated to a small volume. An excess of oxalic acid in sufficient water was added to effect complete solution. No salt separated in the course of several days. The solution was then thoroughly exhausted with ether†, filtered with charcoal, and basified in small portions with ammonia. The liberated base was extracted with ether in which it was sparingly, though completely, soluble. The washed ether solution on partial evaporation deposited colorless stout needles which melted at 114° C. with the evolution of vapors, evidently water. This hydrate, when recrystallized from ether, melted at 115 to 116° C. and slowly lost its water of crystallization at room temperature. It then melted at 137 to 139° C. Total yield, 0.40%.

Caseanine is easily obtained in anhydrous, almost colorless prisms when its solution in benzene, which has been heated to expel water, is cautiously treated with petroleum ether. As thus obtained it melts sharply at 142° C. It dissolves in sulphuric acid to give a colorless solution. On heating, the solution becomes pink and finally brown; this color changes to purple when the solution is cooled. Found: C, 71.03; H, 7.04; N, 3.99; OMe, 33.75%. Calcd. for $C_{21}H_{25}O_4N$: C, 70.99; H, 7.04; N, 3.94; 4OMe, 34.93%.

* *All melting points are corrected.*

† *It has been the experience of one of the authors (R. H. F. M.) that the extraction of oxalic acid solutions with ether is a more effective procedure for purifying crude alkaloids than extraction of mineral acid solutions.*

The *picrate* was recrystallized from hot water containing a little methanol. The pale yellow needles thus obtained melted not quite sharply at 112 to 113° C., and this melting point was not depressed when the substance was admixed with a specimen of aurotensine dimethyl ether picrate.

The hydrochloride is only sparingly soluble in cold water, crystallizing from a hot solution in colorless fine needles.

Alkaloid F33

The fraction (BCE) was dissolved in chloroform-methanol, filtered, and the solution evaporated to a small volume. Colorless fine needles rapidly separated, and these induced crystallization when introduced into a methanolic solution of (EEC). The combined product from the two fractions was redissolved in hot chloroform, in which it is only sparingly soluble. The solution was rapidly evaporated to a small volume and treated with methanol. The base then crystallized at once. After filtering off, washing, and drying, it melted at 257° C. with slight previous darkening. It has a strong tendency to become electrified, and its transfer to a bottle is difficult even in a beam of ultra-violet light. Its empirical formula, its phenolic nature, and the presence of two methoxyl groups indicate that it may be a second di-O-desmethyl-caseanine. Found: C, 69.44; H, 6.69; OMe, 17.40%. Calcd. for $C_{19}H_{21}O_4N$; C, 69.74; H, 6.40; 2OMe, 18.89%.

Casealutine (F32)

The filtrate from the crystallization of alkaloid F 33 on slight evaporation deposited a second base. This was recrystallized from chloroform-methanol and was then obtained in colorless stout prisms which melt to a dark tar at 230° C. The colorless solution in sulphuric acid becomes pink, olive, and finally purple on progressive heating, the last becoming more intense on cooling again. Found: C, 70.14; H, 6.86; N, 4.58; OMe, 26.64%. Calcd. for $C_{20}H_{23}O_4N$; C, 70.38; H, 6.75; N, 4.10; 3OMe, 27.27%.

A small portion of casealutine was suspended in methanol and treated with an ethereal solution of diazomethane. In the course of about ten days the alkaloid was completely dissolved. The solvents were evaporated and the residue was dissolved in dilute hydrochloric acid; this yielded a sparingly soluble hydrochloride. The regenerated non-phenolic base was recrystallized from ether, and thus yielded the sparingly soluble hydrate of caseanine, which either alone or admixed with an authentic specimen melted at 115 to 116° C. The anhydrous base was prepared by recrystallization from benzene-petroleum ether. It melted at 142° C.; admixture with anhydrous caseanine did not depress the melting point.

l-Corypalmine

The mother liquors from the casealutine and especially those from fraction (EEC) after some time deposited a mixture of bases. These were extracted with several successive portions of hot methanol (the residue consisted of impure casealutine) and the extracts evaporated somewhat. The colorless

base which crystallized on cooling was recrystallized from chloroform-methanol, and it then melted at 226° C. when placed in a bath at 210° C. In admixture with a specimen of *l*-corypalmine, which melted at the same temperature and which on methylation yielded *l*-tetrahydropalmatine, there was no depression in the melting point. In admixture with casealutine it was completely liquid at 214° C. The color reactions with sulphuric acid are similar, although when carried out side by side the differences are evident. In the cold acid, *l*-corypalmine yields a colorless solution which on heating undergoes the following color changes,—pale pink, then almost colorless to olive, and finally intense purple, which, on dilution with water, becomes bright orange with a reddish cast.

Alkaloid F34

The more soluble portions of fractions (BCE and EEC) deposited on long standing a further mixture of crystalline bases. A series of fractional crystallizations yielded a more soluble base which was finally recrystallized from chloroform-methanol. The colorless needles appeared completely homogeneous and melted at 218° C., sintering and darkening at a temperature several degrees lower. In admixture with either *l*-corypalmine or with casealutine it was completely liquid below 210° C. Its colorless solution in sulphuric acid became yellow and then pink on gentle warming and brown on heating; on cooling, the solution became purple. The analyses indicate that it is isomeric with casealutine. Found: C, 70.04; H, 6.92; N, 4.28; OMe, 26.65%. Calcd. for: $C_{20}H_{23}O_4N$; C, 70.38; H, 6.75; N, 4.10; 3OMe, 27.27%.

Alkaloid F35

The final mother liquor from (BCE and EEC), which yielded no more crystalline alkaloids, was neutralized with hydrobromic acid and evaporated to a thin syrup. The sparingly soluble hydrobromide which separated in the course of several days was recrystallized from hot methanol-acetone. It was dissolved in hot water, in which it is sparingly soluble, and the rapidly cooled solution basified with ammonia. The crystalline precipitate thus obtained was recrystallized from hot methanol by the cautious addition of hot water. Large, well defined colorless plates melting sharply at 145° C. were thus obtained. No solvent of crystallization appears to be present in the crystals. The alkaloid dissolves in cold sulphuric acid to give a colorless solution which develops a pale pink color on prolonged heating only. Found: C, 70.43; H, 6.84; N, 3.98; OMe, 26.68%. Calcd. for $C_{20}H_{23}O_4N$; C, 70.38; H, 6.75; N, 4.10; 3OMe, 27.27%.

Methylation with diazomethane yielded a methyl ether which when recrystallized from methanol-ether melted at 186° C. It gave the same color reaction with sulphuric acid as its phenolic precursor.

Protopine and α-Allocryptopine

The isolation of protopine in a state of purity is in general a facile procedure. In the present instance no difficulty was encountered in separating it from

the allocryptopine, which appears to be the only other alkaloid in the fraction (BS). The yield of protopine was 0.10%.

A small amount of α-allocryptopine was also obtained from fractions (BC and EC). In all cases the protopine was eliminated as hydrobromide, and the purified α-allocryptopine melted at 160° C. Comparison with an authentic specimen failed to reveal any differences. The yield was 0.16% and this is the only plant, in so far as the authors are aware, in which the amount of allocryptopine is greater than that of protopine.

l-Scoulerine

The fractions (BSE and EES) in contact with methanol yielded a small amount of alkaloid F33. The filtrate from the latter was neutralized with hydrochloric acid and evaporated to a small volume. A sparingly soluble hydrochloride readily crystallized. The free alkaloid was regenerated from this and recrystallized from methanol-ether. It melted at 193 to 194° C. and in admixture with an authentic specimen of *l*-scoulerine from *C. scouleri* it melted at 194° to 195° C. The entire specimen, which weighed approximately 50 mg., was methylated with diazomethane in methanol ether. The non-phenolic base thus obtained when recrystallized from ether melted sharply at 142° C. either alone or in admixture with a specimen of *l*-tetrahydropalmatine.

Fumaric Acid

The isolation of pure fumaric acid from the fraction (LC), as in previous cases, was relatively simple, although the amount present is probably not more than 0.1%.

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LINOLEIC ACID AND ITS ISOMERS[1]

By J. W. McCutcheon[2]

Abstract

Linoleic acid has been prepared from sunflower seed oil by a modification of Rollett's method. The melting point of the solid tetrabromostearic acid is placed at 115.2° C. The boiling point, specific gravity, iodine value, and refractive index of the ethyl ester and the melting point of the free acid were determined. Linoleamide was prepared, and its melting point is placed at approximately 58° C. Through rebromination of the prepared linoleic acid, the isomeric liquid tetrabromostearic acid was isolated, and is described. Its reduced acid is shown to be identical with that derived from the solid isomer. From these data and additional data from the literature, it was concluded that bromination and debromination cause no *cis-trans* isomerization, and that the two pairs of optically active enantiomorphous bromo derivatives exist, not because of their derivation from different acids, but rather because of the four asymmetric carbon atoms which they contain. Therefore, only one naturally occurring linoleic acid is at present known which is identical with that produced through reduction of the tetrabromide that melts at 115.2° C. or the corresponding liquid derivative. No attempt is made to assign any particular *cis-trans* configuration to this acid, or to exclude the theoretical existence of three others.

An investigation of the hydrogenation process as applied to vegetable and animal oils was carried out recently by the author. A review of the literature revealed the problem to be very complex, largely owing to the difficulty of obtaining elementary pure raw materials. Linoleic acid is the most common and simplest acid available for the study of selective hydrogenation, but it has been used very little, possibly owing to the difficulty of preparation and the uncertainty regarding the product obtained. The work of those who did use it was open to the criticism that the product was not pure (23) or did not represent the natural acid (20). Hence, it was suggested that, as a preliminary to the further study of hydrogenation, an investigation be conducted on the preparation of this acid, with the object of obtaining it in a pure state and studying its isomerism.

Linoleic acid occurs to the extent of about 25 to 50% in the semidrying oils such as cottonseed, peanut, soybean, and others. It has been shown by Hilditch and Vidyarthi (7), Riebsomer and Nesty (16), Smit (20) and others, chiefly through oxidation reactions, to be the $\Delta^{9,12}$ octadecadienoic acid, of which, according to Inoue and Suzuki (9), four possible *cis-trans* isomerides should exist.

Up to the present, the method of Rollett (17) has been the only one available for the preparation of this acid in any degree of purity, although very recently several interesting papers have appeared that suggest the use of freezing mixtures (3, 4). Rollett's method depends on the bromination of the liberated fatty acids of the oil, the separation of the solid tetrabromostearic acid, and its subsequent reduction by means of zinc. That these operations cause no

[1] *Original manuscript received July 21, 1937.*
Contribution from the Department of Chemistry, University of Toronto, Toronto, Canada. From a thesis presented in partial fulfilment of the requirements for the M.A. degree at the University of Toronto.

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bond shift has been shown by Smit (20), Suzuki and Inoue (21), Hilditch and Vidyarthi (7), Hilditch and Green (6), and others, although it has been apparent from the first that stereoisomerism does occur, since less than 50% of the theoretical quantity of the solid tetrabromide is precipitated. Only two isomers, a solid, m.p. 113° to 115° C., and a liquid, exist, the proportions formed being generally given as 40 to 50% solid and the remainder liquid (6, 14, 17, 22).

It was suspected for some time that a third (22) and even a fourth (18) isomer did exist. These were shown by Palmer and Wright (15) and later by Smit (20) to be merely the ethyl or methyl ester of the tetrabromide, formed during crystallization.

The so-called solid, or α-tetrabromide, is a snow white, crystalline compound readily soluble in sulphuric ether, alcohol, glacial acetic acid, and other solvents, but sparingly soluble in petroleum ether. Its melting point has been generally recorded as 113° to 115° C. (11, p. 202; 17, 22), but one result places it at 116° to 117° C. (20).

The liquid, or β-tetrabromide, differs from the solid in its ready solubility in petroleum ether. Both these tetrabromo compounds when reduced to the acid and rebrominated yield further mixtures of the same two isomers.

The solid isomer yields on reduction α-linoleic acid, which is generally considered to be identical with the naturally occurring product; both give on mild oxidation the same two sativic acids, m.p. 155° and 173° C. (6). As far as can be learned, no data regarding the acid or esters from the liquid tetrabromide have been published, with the exception of those of Hilditch and Green (6), who report finding very small amounts of the same sativic acids as obtained from the solid derivative.

Rollett believed that there occurred only one linoleic acid which gave two bromo derivatives, each representing a racemic compound. Hilditch and Green (6) also believed that only one natural linoleic acid is present in seed fats, as does Smit (20), who added, however, the opinion that the bromination probably causes a Walden inversion, so that the derived product may not be the same as the natural one. Nicolet (13) believes that isomerization occurs in bromination, and thus accounts for the two tetrabromides as being produced from two or even more linoleic acids. In conclusion, it may be mentioned that van Loon (12) and van der Veen (24) point out the fallacy of designating the derived acids from the α- and β-tetrabromides with the same appellation because of the isomerism known to occur.

The investigation described herein had for its object *(a)* the establishment of additional constants of the esters of the solid tetrabromo derivative, and *(b)* the preparation of the liquid derivative in a state pure enough for its comparison with the solid derivative.

Experimental Data

The Raw Material

Sunflower seed oil was chosen not only because of its exceedingly high content of linoleic acid, but also because of the complete absence of linolenic

or more highly unsaturated acids. The analyses given in Table I, except for a rather high unsaponifiable content, closely correspond to the normal values for such an oil.

TABLE I

ANALYSIS OF THE SUNFLOWER SEED OIL USED

Free fatty acid (as oleic, refined oil), %	0.07	Analysis of the fatty acids, %	
Color	4.5 red/35.0 yellow		
Iodine value (Wijs)	128.2	Saturated acids (Twitchell)	10.0
Saponification value	193.4	Oleic acid (by calculation)	31.0
Total fatty acids, %	95.6	Linoleic acid (by calculation)	57.2
Hexabromide test (absence of linolenic acid)	Negative	Unsaponifiable	1.8
Unsaponifiable, %	1.78		
Iodine value of unsaponifiable	149.7		

Preparation of the Fatty Acids

In the preparation of the fatty acids the method recommended by the American Oil Chemists' Society (1) was closely followed, the usual care being taken to avoid oxidation. Yields of 90 to 92% were readily obtained, and the product was preserved in an atmosphere of carbon dioxide.

The Bromination

The bromination, debromination, and esterification were carried out in a manner similar to the method of Rollett (17), the main differences being; (i) the bromination was carried out at 20° to 25° C. rather than at zero; (ii) a special purification process for the solid tetrabromide was introduced; (iii) debromination and esterification were carried out as two separate steps; (iv) the esterification was completed in the absence of zinc.

A solution of 30 ml. of liquid bromine in 400 ml. of petroleum ether was sprayed into a mixture of 100 gm. of the fatty acids and 1600 ml. of the ether over a period of about 15 to 20 min., the temperature being held between 20 and 25° C. The petroleum ether (b.p. 40° to 60° C.) conformed to the standards required in extraction work by the methods of the American Oil Chemists' Society (1). Table II indicates the yields obtained in the bromination of various batches.

TABLE II

YIELDS OF SOLID TETRABROMIDE OBTAINED FROM VARIOUS BATCHES

Batch	Weight of oil taken, gm.	Weight of tetrabromide, gm.	Corr. m.p., °C.	Yield, % of theoretical
1	100	48.9	112.6	36.2
2	100	48.8	113.0	36.2
3	100	57.0	114.0	49.1*
4	1060 (5 batches)	465.5	114.1	36.5†
5	20 (pure linoleic acid)	20.4	114.2	47.6*

** High yield due to the use of tetrabromide-saturated petroleum ether and the residue-containing beakers from previous batches.*

† This batch was prepared in April, 1936.

Through subsequent work on the solubility of the tetrabromide in petroleum ether, the true yield is believed to be 50% of theory. This is obtained by allowing a solubility of 2 gm. of the bromide in 1000 ml. of petroleum ether, and adding a manipulative loss of 12%. This conclusion appears justified by the findings with Batches 3 and 5.

Purification of the Tetrabromides

A pilot lot of 10 gm. was refluxed for one hour at 47° C. with petroleum ether, filtered, dried, and screened. A second lot was treated similarly twice. Both products had identical melting points (114.7° C.*), which checked well with the value (114.6° C.) obtained in the previous year.

However, in some experiments conducted at this time to determine the solubility of the tetrabromide in boiling petroleum ether, it was noted that the filtrate from some of the hot solutions showed definite, needle shaped crystals. By reworking these, about 1 or 2 gm. of beautifully crystalline needles, which formed in clusters, was obtained. Under the high power microscope they were found to be transparent and somewhat square at the ends. It was concluded that this product would be exceptionally suited to the checking of the true melting point of the tetrabromide. The results on this sample were 115.2, 115.2, 115.1, 115.2 (very fine capillary), 115.2 (closed tube method). Average, 115.2° C.

From this work it was concluded that the solid tetrabromide could not be sufficiently purified by simply washing it with petroleum ether. After several trials with small pilot batches, the following methods were adopted and applied successfully not only to the material that melted at 114.7° C. but also to the residues from Batch 1 (m.p. 112.6° C.) to raise the melting point to 115.1° C. The yield for each crystallization was about 80%. However, there is no doubt that greater yields could be obtained with larger batches.

Method 1

To 15 gm. of the tetrabromide in a 2000 ml. beaker was added 600 ml. of petroleum ether. The height to which the solvent rose was marked so that a correction could be made for losses during boiling. The mixture was brought to a vigorous boil on a water bath, and then just sufficient absolute ethyl alcohol to completely dissolve the whole precipitate was added slowly. Repeated experiments gave values very close to 5% by volume (30 ml.) under these conditions. The hot solution was filtered with suction through a 4 in. Büchner to remove any foreign material, and it was then chilled to 0° C. The chilled solution was filtered and washed with 300 to 400 ml. of fresh petroleum ether.

The color of the filtrate indicates whether one crystallization is sufficient. Owing to the fine, easily broken down texture of the material, it is not necessary to screen the product. Altogether, 80.8 gm. of the compound was so prepared.

Although this method was satisfactory with a well washed crude material of melting point 114.5° C. or higher, the low temperature crystallization was

* *All melting points determined by the author are corrected.*

not very satisfactory for materials less pure, since there was a tendency for the liquid tetrabromide to co-precipitate. Method 2, suggested by the work of Smit (20), was developed in order to obviate this difficulty.

Method 2

Tetrabromide (100 gm.) was dissolved in 200 to 300 ml. of sulphuric ether and filtered. The ether was then evaporated to incipient crystallization (about 100 ml.) and diluted with petroleum ether to about 1500 ml. The solution was then cooled to 15° to 20° C., filtered, and washed. Yields approximated 70 to 80%.

The purified crystals are snow white, and have a slight silver sheen. When viewed under the high power microscope they appear as long narrow rectangular plates with square ends. With lower magnification they appear needle shaped. They melt without decomposition to a pure white solid, but traces of impurity will cause a decided browning. The bromine content was 53.20%; theoretical, 53.28%.

Solubility of the Tetrabromide in Petroleum Ether

Although this was not intensively studied, experiments indicated that the solubility varied from about 0.4 gm. per 100 ml. at 45° C. to about 0.1 gm. at 0° C. Solutions showed a great tendency to become supersaturated even in the presence of excess tetrabromide.

Debromination and Esterification

The debromination was carried out with 40-gm. lots of the tetrabromide in 300 ml. Erlenmeyers, about 35 gm. of 20 mesh zinc metal being used. After the first vigorous exothermic reaction was over, the whole was refluxed 30 min. before any alcoholic hydrochloric acid was added. Esterification was carried out in the usual manner with 4 *N* alcoholic hydrochloric acid for two hours. The zinc was then removed, and the solution refluxed for an additional hour. The color of the product during these operations will vary from pale straw to water white, depending on the purity of the tetrabromide used. The ester was separated with a brine solution, washed, filtered, and distilled under high vacuum. The product was a water white liquid. Yields obtained with a number of batches are given in Table III.

TABLE III

YIELDS OF ETHYL LINOLEATE FROM TETRABROMOSTEARIC ACID

Weight of tetrabromide used, gm.	40	100	93.6	171.9
Weight of ethyl ester recovered, gm.	16.7	42.2	42.1	74.0
Yield, % of theoretical	81.3	82.4	87.9	84.4

The product distils at constant temperature without the formation of any residue, and the acidity should be less than 0.25% calculated as linoleic acid.

The acid is obtained from the ester, as required, by the method of cold saponification outlined by Rollett (17). Except for the 50% loss of tetrabromostearic acid by the formation of the liquid isomer, the yields vary from

about 80 to 90%, depending on the number of manipulations involved. From the accumulated data of experiments with numerous batches, the yields given in Table IV may be expected.

TABLE IV

SUMMARY OF TYPICAL YIELDS—SUNFLOWER SEED OIL TO LINOLEIC ACID

Substance used	Amount, gm.	Substance obtained	Amount, gm.
Sunflower seed oil	100	Fatty acids	87
Fatty acids	87	Tetrabromide	42.5
Tetrabromide	42.5	Purified tetrabromide	35
Purified tetrabromide	35	Distilled ethyl ester	14.6
Distilled ethyl ester	14.6	Linoleic acid	12.5

It was observed that, as compared with the free acid, the pure ester was an extremely stable compound. The iodine value, refractive index, and color samples kept in ordinary two ounce white-glass bottles for more than a year at room temperatures remained virtually unchanged. For this reason it was considered advisable to determine, as far as possible, the constants of the ester rather than of the free acid. The following are a few of the constants that have been determined:—ethyl ester—the boiling point, specific gravity, refractive index, and iodine value: free acid—the melting point. The linoleamide was prepared from the free acid.

The Boiling Point of the Ethyl Ester

The distilling apparatus consisted of two Pyrex 50 ml., round bottomed flasks so joined together by a short piece of 8 mm. Pyrex tubing that one might be used as the distilling flask and the other as the receiver, alternately (Fig. 1). Thus it was possible to repeat conveniently the determinations with the minimum loss in transfer, and also to check whether any decomposition was taking place.

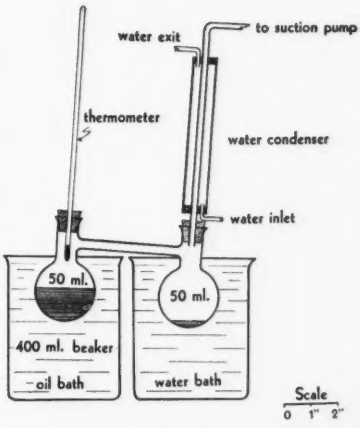


FIG. 1. *Distilling apparatus.*

The vacuum gauge was of the Bennert mercury manometer type with movable milk glass scale, 13 cm. each way from zero, *i.e.*, a 0 to 260 mm. range. The readings were taken with the aid of a three-inch reading glass, and the observer checked his method of reading the meniscus by taking the zero reading on the manometer alone.

The vacuum control apparatus as constructed was identical with that described by Schierholtz (19). After a preliminary adjustment no difficulty

was experienced in maintaining the vacuum at various values between 1 and 20 mm. of mercury with no observable fluctuations in the meniscus.

The temperature was taken with an ordinary −10° to 360° C. mercury thermometer, which was graduated in 1° C. divisions. The over-all length was 16 in., with 27° to the inch. It was checked against a thermometer supplied with a U.S. Bureau of Standards' certificate and table of corrections. At temperatures 197°, 202°, and 206° C. no differences could be noted between the thermometers when the corrections were made. The effect of a vacuum on the bulb was studied by setting up the unit in a water bath held at a very definite temperature close to that of the room, and reading the thermometer before and after the pressure was reduced to 1 mm., due care being taken to allow the heat developed to be dissipated. The correction caused by expansion of the bulb under such reduced pressure was found to be 0.2° C., and was therefore neglected in subsequent work.

Operation

The distilling flask was heated in an oil bath. No bumping occurred except at a pressure of 17 mm. Bumping was probably minimized by the design of the apparatus which permitted no drops to form on the outlet tube. A very slight rise in temperature was noted toward the end of the distillations; this was attributed to the gradual increase of vapor head in the flask. For this reason the flasks were reversed when about two-thirds of the product had distilled over.

An assistant aided in recording the data; this made the simultaneous recording of pressure and temperature possible. The distillation was maintained for several minutes until the temperature and pressure became constant. Finally, after a series of increasing pressures, the original low pressure was restored in order that a possible change in boiling point due to decomposition could be checked. No change was noted. The data obtained are given in Table V.

TABLE V

BOILING POINT DATA FOR ETHYL LINOLEATE, TAKEN AT VARIOUS REDUCED PRESSURES

Pressure, mm.	2.5	4.5	6	12	17	2.5
Temperature uncorrected, °C.	171.0	184.0	190.5	208.5	220.0	170.5
Temperature corrected, °C.	175	187.5	193.5	212	224	173

Final values are given to the nearest one-half degree. None of the previous values obtained by the author under less exacting conditions differ by more than a very small fraction from the values given in Table V. These results are presented graphically in Fig. 2.

Specific Gravity of the Ethyl Ester

The specific gravity of the ethyl ester was determined in the usual way with a 10 ml. Gay-Lussac type specific gravity bottle that had been standardized with freshly boiled distilled water. Thermometer and weights were checked against standard equipment, and the necessary corrections made. The data and results are given in Table VI.

TABLE VI

SPECIFIC GRAVITY OF ETHYL LINOLEATE

——	Temp., °C.	Grams	Specific gravity
Air wt. of pycnometer (P)		8.0004, 8.0004	
P + water	15.5	17.9769, 17.9768	Apparent, 0.8844 (15.5°/4° C.)
P + water	25.0	17.9594, 17.9596	True, 0.8846 (15.5°/4° C.)
P + ester	15.5	16.8323, 16.8323	Apparent, 0.8775 (25.0°/4° C.)
P + ester	25.0	16.7652, 16.7652	True, 0.8776 (25.0°/4° C.)

Humidity, 50%; brass weights, density 8.4.

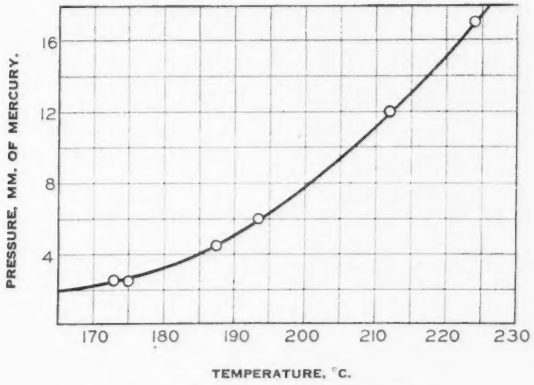


FIG. 2. *Boiling point curve of ethyl linoleate.*

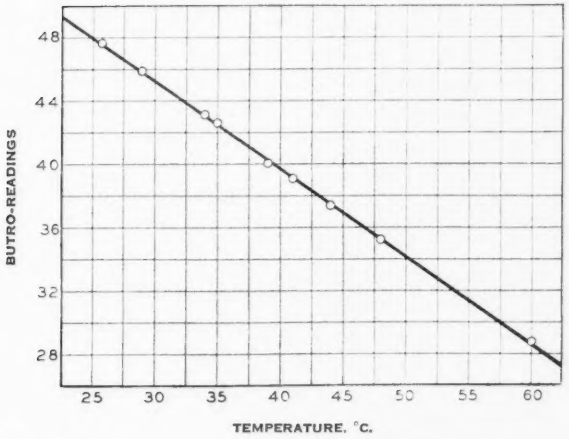


FIG. 3. *Butro-refractometer readings for ethyl linoleate at various temperatures.*

Refractive Index of the Ethyl Ester

The refractive index was determined by means of a butro-refractometer, with light filtered through a dichromate solution so as to approximate sodium light. The results are presented in Table VII, and graphically in Fig. 3.

TABLE VII

REFRACTIVE INDEX OF THE ETHYL ESTER OF LINOLEIC ACID

Temp., °C.	25.8	29.0	34.0	35.0	39.0	41.0	44.0	48.0	60.0
Butro-reading	47.70	45.85	43.10	42.60	40.25	39.10	37.40	35.20	28.75
Refractive index	1.4578	1.4565	1.4546	1.4542	1.4526	1.4518	1.4505	1.4489	1.4443

NOTE:—*Temperatures were read to 0.1° C., but in controlling the rise in temperature it was convenient to hold them at the even values.*

The values 1.4488, 1.4491, and 1.4486 were obtained for the refractive index at 48.0° C. of three lots of esters that were prepared the previous year.

Iodine Value

The iodine value of the ethyl ester, as determined by means of the Wijs method (1), was *(a)* 162.29, *(b)* 162.49; average, 162.39. These results agree well with those of Rollett (17) and van der Veen (25).

The Melting Point of Linoleic Acid

Ordinary melting point tubes were filled with linoleic acid and immersed in a beaker of alcohol chilled with solid carbon dioxide to about −65° C. The acid froze immediately to a white solid. By transferring the tubes to an alcohol bath at −30° C. and allowing the bath to warm gradually, a fairly sharp melting point was noted between −8° and −9° C., with duplicate samples prepared from different batches of the ethyl ester. One of these samples, however, after standing for several days in an atmosphere of carbon dioxide, was observed to have a melting point of −13° to −14° C. A fresh sample again gave the melting point of −8° to −9° C., which did not change when the sample, in the form of a thin film, was exposed to the atmosphere for 30 min. Lewkowitsch (11, p. 184) has suggested that oleic acid is dimorphous, having melting points of about 4° and 14° C. Possibly linoleic resembles oleic in this respect, and indeed both values, approximately, have been reported by different workers (8, 20).

In an endeavor to settle the above question an attempt was made to study the transition points by means of the dilatometric method (5, p. 274). The attempt was unsuccessful, but it is hoped that this work will be pursued at a later date.

Linoleamide and Its Preparation

Linoleamide was prepared according to the method of Aschan (2). After a number of preliminary experiments with pure oleic acid from which crude oleamide of melting point 72° to 73° C. was obtained, a small pilot batch of linoleamide was prepared (m.p. 57° C.). Both the oleamide and the linoleamide were soft, soapy, non-crystalline substances, very difficult to filter. The details of the preparation follow.

Ten grams of the linoleic acid was weighed into a four ounce glass-stoppered bottle and 2 ml. of phosphorus trichloride added. The mixture was shaken at intervals for several hours and allowed to stand overnight. The supernatent acid chloride was then transferred to a small glass-stoppered dropping funnel and slowly run into about 400 ml. of well agitated concentrated ammonia solution held at 0° C. in an ice bath. The ammonia solution was diluted to about four times its volume with distilled water and extracted with chloroform. The solvent was distilled off and the oily residue (about 5 ml.) was taken up with about 75 ml. of absolute ethyl alcohol, and filtered.

The filtrate was chilled until about 75% or more of the solid had precipitated. A small portion was laid aside for melting point determination, and the remainder was again dissolved and reprecipitated, m.p. 57° to 58° C.

After several days the soapy material in all samples had separated into two phases: a substance having a fibrous structure, and an amber liquid. The possibility of the presence of two isomers became apparent. After five weeks, however, a careful microscopic examination of the liquid and solid phases failed to reveal any crystalline structure. In fact, the fibrous material was found to be in a state of gradual decomposition. The conclusion reached was that only one substance was originally present, but that on standing it gradually oxidized and polymerized. The sample had been kept in a small glass-stoppered bottle, and it was not considered likely that sufficient oxygen was present to cause the complete change observed.

The Preparation of the Liquid Tetrabromide

Since the liquid tetrabromide can be obtained only by difference, considerable care must be taken to use nothing but pure linoleic acid as starting material. Twenty grams of the linoleic acid was prepared from the 43 gm. of triple-distilled ethyl ester as described previously. It was brominated in the usual manner except for the following differences:—

(a) The petroleum ether was the recovered material from previous brominations, so as to insure against the possible formation of non-volatile bromo addition products. In addition a small blank was run for such residues. None was found.

(b) The temperature of bromination was held from −10° C. at the beginning to −2° C. at the end.

(c) The amount of bromine was increased from 6 to 10 ml.

The solid tetrabromide was filtered in the usual way and washed with three lots of 300 ml. of petroleum ether cooled to −20° C. It was quite granular and easily worked over. The melting point of the crude tetrabromide was 112.7° C.; that of the recrystallized tetrabromide was 114.8° C. The yield was 20.0 gm.

The filtrate was then chilled to −20° C., whereupon a brown gummy viscous material began to separate out; it did not completely redissolve until the temperature had risen to −10° C. At 0° C. a small, hard, horny mass still remained undissolved; when this was filtered off, dissolved in boiling

petroleum ether, and chilled again to $-20°$ C. a fine white material that was identified as the solid tetrabromide was obtained. Yield, 0.3 gm.

The main filtrate was then chilled to approximately $-65°$ C. in an alcoholic bath containing solid carbon dioxide. The liquid tetrabromide formed a thick viscous layer on the sides and bottom of the beaker. The solid tetrabromide still remaining in solution formed a fine white suspension, which was readily removed by filtration. Yield, 0.1 gm.

Total yield of solid tetrabromide:— $20.0 + 0.3 + 0.1 = 20.4$ gm., equivalent to 47.6% of the theoretical.

The liquid tetrabromide remaining in the bottom of the beaker was dissolved in fresh petroleum ether and transferred to a 250 ml. Soxhlet flask. By alternately warming and chilling to about $-65°$ C. it was possible to wash the liquid compound by decantation. After the first wash the filtrates were almost colorless. The final product was a pale straw colored viscous syrup. The first filtrate when concentrated also gave a similar product in almost equal quantity; this indicates that even at $-65°$ C. the liquid tetrabromide is considerably soluble in petroleum ether.

The total weight of liquid tetrabromide was 12.1 gm., although no attempt was made to obtain a quantitative yield. From this, 3.4 gm. of the ethyl ester was prepared in the usual manner, and its boiling point determined. This was repeated on a larger scale, 25.2 gm. of ethyl ester being prepared from the tetrabromide that melts at 115.0° C. After the solid isomer had been filtered off at $-1°$ C., the liquid was obtained by evaporation of the petroleum ether under a current of carbon dioxide gas. The yield was 25.1 gm., or 49.2% of the theoretical. This product was esterified in the usual way, no difficulty being experienced, and distilled three times; a water white liquid was obtained. The constants determined for these compounds are compared in Table VIII with previous values obtained for the solid tetrabromo derivative.

TABLE VIII

COMPARISON OF SOME PHYSICAL CONSTANTS OF ETHYL LINOLEATE PREPARED FROM BOTH THE SOLID AND THE LIQUID TETRABROMOSTEARIC ACID

Lot	Boiling point values				Refractive index (25.1 gm. lot)			
					Liquid tetrabromo derivative		Solid tetrabromo derivative	
	Pressure, mm.	Ester from liquid tetrabromide, °C.	Ester from solid tetrabromide*, °C.	Temp., °C.	Butro-reading	Refractive index	Butro-reading	Refractive index
3.4 gm.	5	190	190	48.0	35.05	1.4488	35.20	1.4489
3.4 gm.	12	215	212	38.0	40.60	1.4528	40.72	1.4529
25.1 gm.	11	208.5	209					

True specific gravity (15.5°/4° C.) of ethyl ester is:— 0.8845, liquid derivative; 0.8846, solid derivative.

* *See Fig. 2.*

The constants given in Table VIII agree within the limits of experimental error and point to the identity of the products. It is to be noted that the refractive index of the liquid tetrabromo derivative is lower than that of the solid, as would be expected, since it contains the accumulated impurities.

In addition, the liquid tetrabromide was prepared from the 35.4 gm. lot of ester obtained during April of 1936. A modification consisting in the removal of the excess bromine by shaking out with thiosulphate solution followed by thorough washing was introduced. Both liquid bromides were pale straw colored liquids that set to a semi-solid mass on standing overnight. They had a peculiar varnish-like odor. Some acrolein, which was finally traced to the petroleum ether, was present in each liquid. Although this would have no effect on the ester derivative, it was considered advisable to repeat the preparation of liquid tetrabromide to decide whether the crystallization observed after standing was caused by such impurities.

Petroleum ether of boiling point 30° to 55° C. was brominated and distilled. A 100 ml. sample of this material was then rebrominated and redistilled. No residue remained at 60° C. and there was only a very faint odor suggesting acrolein. A portion (15.0 gm.) of the 40.2 gm. lot of linoleic ethyl ester prepared during April, 1936, was saponified and brominated in the usual way. The solid tetrabromide was filtered off, and the filtrate chilled to −5° C. and refiltered. The excess bromine was boiled off and the ether solution concentrated to about 30 ml. It was then chilled to about −65° C. in an alcohol bath containing solid carbon dioxide, whereupon the liquid tetrabromide separated out as a thick milky gum adhering to the walls of the beaker. The ether was poured off, and fresh ether added. In this manner the bromide was washed three times by decantation. It was then transferred to a 25 ml. ampoule, and the final traces of solvent were removed by warming under a pressure of $\frac{1}{2}$ to 1 mm. The product darkened somewhat during the latter process, but it was considered advisable to ensure the removal of acrolein should any be present. The ampoule was then sealed off under a pressure of 1 mm. or less.

The warmed material was a dark pale straw colored substance resembling melted rosin. When the ampoule was immersed in a bath at −65° C. for a few minutes, the bromo compound became solid, and fractured along the walls of the tube. These fractures disappeared almost immediately on removal of the tube from the cold bath. The tube was rotated and the material thus spread in a film over the surface of the tube, which was then chilled, but crystallization did not occur. After the material had stood at room temperature for 24 hr., however, crystals appeared. The conclusion was then drawn that this phenomenon was not due to impurities as originally suspected. The bromine content was found to be 53.12%, theoretical 53.28%. When the acid from the liquid derivative was again brominated, the yield of solid tetrabromide was that usually observed.

Discussion of Results

The Melting Point of the Solid Tetrabromostearic Acid

The melting point of the solid tetrabromide has been placed by the author's work at 115.2° C., a value close to that generally accepted. With many samples of crude material the author has obtained values ranging from 113° to 114.7° C., which, with some samples, could not be raised after repeated pulverizing and washing. Without recrystallization the maximum melting point obtained for any sample was 114.7° C. On the other hand, with only one recrystallization the minimum value obtained was 114.7° C., and the maximum, 115.1° C., although all values were obtained with fairly large batches. This possibly explains the variations previously recorded in the literature. The value 116° to 117° C. given by Smit (20) appears to be too high. He used, as raw materials, oils known to contain linolenic acid. Since this acid also forms liquid stereoisomers with bromine, the difficulty of completely removing them by precipitation can be appreciated. That traces of these acids probably contaminated Smit's tetrabromo compound is indicated by the abnormally high iodine value recorded for both the acid and the ester: 181.9 (theoretical 181.1) and 174.4 (theoretical 172.5) respectively. That substitution of bromine in the acid was not the cause of the present author's lower result was carefully ascertained by running a separate test wherein this possibility was reduced to a minimum, by keeping the time of contact between bromine and acid down to five minutes and the temperature from −10° C. at the beginning to −2° C. at the end. The resulting crude material was identical in melting point with that of other batches.

The Iodine Value

The iodine value obtained is somewhat lower than the theoretical, but the author feels that this is no indication of impurity since the values agree very closely with those of Rollett (17) and van der Veen (25). This finds support in the work of Waterman and co-workers (26), and, more recently, in that by de Kok, Waterman and Westen (10), who indicate that the iodine value is always lower than the theoretical unsaturation as measured by the hydrogen absorption.

Isomerism

As regards the isomerism in the bromo compounds, the author presents a few deductions on the mechanism of the change which have been brought to a focus partly through the work described in the present paper, and partly through the accumulated data in the literature.

Granted that isomerization does occur, we may conclude that it does so either in the bromination, in the debromination, or in both.

If isomerization occurs during the debromination process only, we would have to conclude that two naturally occurring linoleic acids exist in various oils as 1 : 1 mixtures. The prepared linoleic acids from the tetrabromides would also then be 1 : 1 mixtures. In view of the uniformity in the boiling

points of various samples of the ethyl ester, the constant yield under varying conditions of bromination, and the fact that only one linoleamide is produced, it is difficult to believe that such a condition does exist.

If isomerization occurs both in the bromination and the debromination processes, then, in order that both acids derived from the solid and liquid bromo compounds be identical, it would follow again that both the natural and derived linoleic acids would be 1 : 1 mixtures of two isomers, and the same objections mentioned above would apply. It would also be necessary in the latter case to assume a very complicated system of conversion.

If isomerization occurred during the bromination process only, we would be forced to conclude that the debromination of each would produce different isomeric linoleic acids, a fact not substantiated by the present work, unless the isomerides occurred only in the bromo compounds and disappeared on their reduction. Now it is very difficult to conceive of a *cis-trans* isomerization that would fulfil this condition, and indeed there is considerable evidence to show that we are not here dealing with such a type. For example, Nicolet (13) has shown that when oleic and elaidic acids (known *cis-trans* modifications) are brominated and debrominated they regenerate their respective parent acids only. Bromination and debromination of these acids thus do not cause *cis-trans* isomerization. In addition, it has been shown by Hilditch and Green (6) that when oleic acid is oxidized with alkaline permanganate solution it yields an hydroxy acid of melting point 132° C., whereas if it is oxidized with hydrogen peroxide in acetic acid, it yields an acid of melting point 95° C. Elaidic acid, the *cis-trans* isomeride, however, yields with permanganate an acid that melts at 95° C., and with peroxide an acid that melts at 132° C. It may be concluded, then, that one of these reagents has caused a *cis-trans* isomerization. Now it is generally agreed (6, 11, p. 203; 22) that natural linoleic acid and the acid derived from the solid tetrabromostearic acid yield on mild oxidation with alkaline permanganate two sativic acids of melting points 173° and 155° C. If now these two acids are *cis-trans* modifications resolvable into each other, then it would be expected that the peroxide oxidations should yield two acids of similar melting points. This is not so, however, as is shown by Hilditch and Green (6). The product obtained is a mixture of two new sativic acids of melting points 146° and 126° C. (Table IX).

TABLE IX

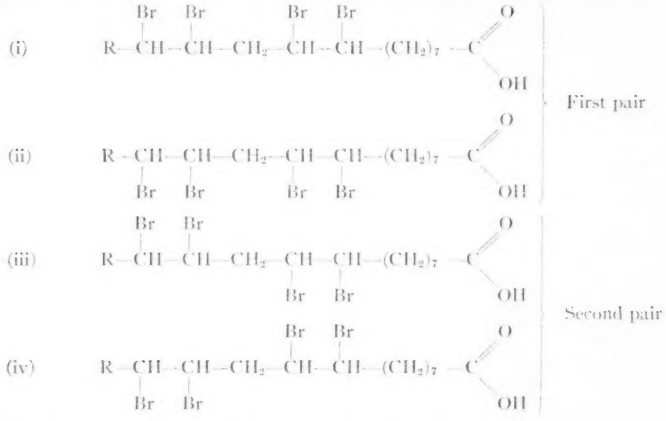
SOME HYDROXY ACIDS AND THEIR MELTING POINTS

Starting material	Melting points (°C.) of the hydroxy acids produced by	
	Alkaline $KMnO_4$	H_2O_2 in acetic acid
Oleic	132	95
Elaidic	95	132
Linoleic	155 173	146 126

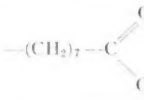
For the above reasons then we will abandon the idea that the transformation observed is of the *cis-trans* type. If now we examine the structure of linoleic

acid by means of a model, it will be seen that there is the possibility that the bromine may enter the compound in four different ways, forming two pairs of optically active compounds, which in no way interfere with the *cis-trans* arrangement chosen or the conception of free rotation in the bromo compounds. If we conceive of the possibility of the bromine breaking the double bond either up or down, independently, we may obtain a rough picture of the thought in mind. Smit (20) made a vague reference to such a conception when he drew attention to the fact that after one double bond is oxidized, isomerization may occur in the manner in which the second one is filled. He did not however consider this from the viewpoint of transformation in the bromo or hydroxy compounds only, but rather in the light of a Walden inversion, which of course would imply isomerization of the reduced compounds as well.

The following formulas and figures partly illustrate this conception:



In the figures of the models, Figs. 4 and 5, the CH_3—$(CH_2)_7$— group is represented by a blue ball, marked *B*, and the



group by a green ball marked *G*. In both models the double bond has been split and the bromine atoms (yellow) added on. Fig. 4 illustrates (i) and (ii), where all the bromines lie on one side of the molecule; Fig. 5 illustrates (iii) and (iv).

It should be noted that in the preparation of the models a *cis-trans* form must be chosen and maintained. The convention has been adopted that when the two bromines are removed and the bonds joined, two white balls or hydrogen atoms on the same side represent a *cis*-form. In the above case the models are of the *cis-cis* type.

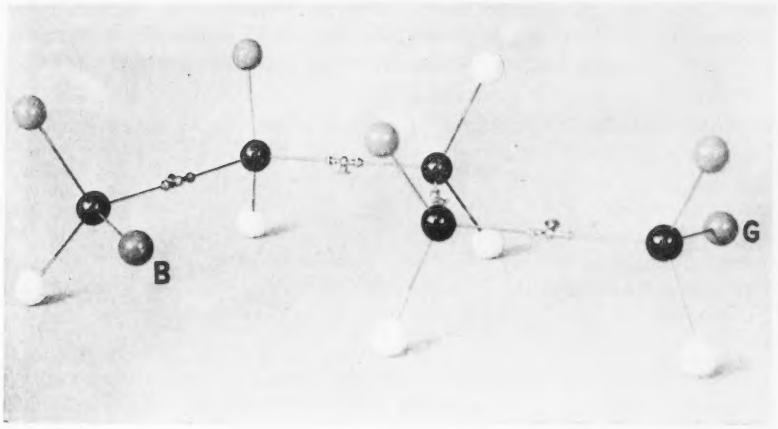


FIG. 4

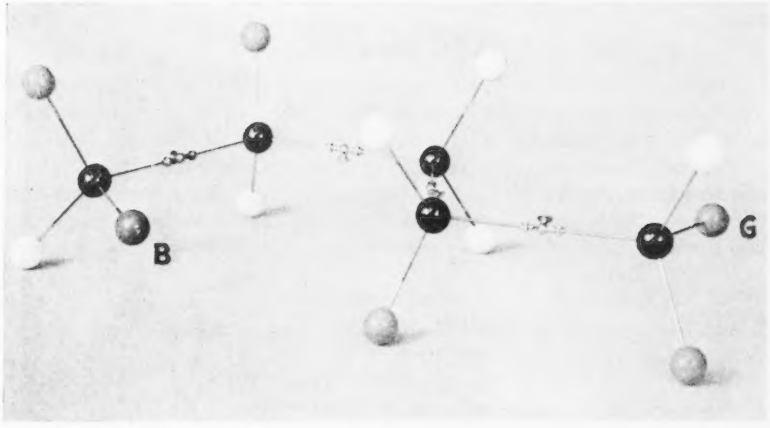


FIG. 5

Possibly the liquid tetrabromide possesses the bromines in line as in the first pair of acids ((i) and (ii)), thus allowing a packing of the molecules in a polymerization and slow crystallization effect. This would account for the wide differences in the physical properties of the solid and liquid compounds. Since debromination would regenerate the parent acid, it explains why both bromo compounds yield identical linoleic acids, and also offers an explanation for formation of equivalent amounts of the isomers in each case. It would then follow that only one natural linoleic acid exists which is identical with

that formed by the debromination of either tetrabromostearic acid. The terms α and β when applied to the solid and liquid tetrabromo compounds would still be valid, but meaningless when applied to the derived acids.

This conception would also allow of the formation of only one bromide of oleic acid and two of linoleic, a conception substantiated by experimental data. It would predict four from linolenic acid. Although four such isomers have not yet been isolated, it is significant that yields of only 23 to 24% of solid hexabromide have been obtained by the bromination of this acid (11, p. 211). Since derived products would have the same opportunity for isomerization, only one hydroxy derivative from oleic acid and two from linoleic would be expected. This is confirmed by the data. It would predict the existence of four hexahydroxystearic acids from linolenic, but this has not yet been confirmed.

In conclusion, the author wishes to acknowledge his indebtedness to the large amount of work done by others in this field, and hopes this paper may stimulate further interest in the subject. The problem as to whether linoleic acid is dimorphous, whether the solid tetrabromide is resolvable into a mixture of two optically active isomers, or whether four isomeric hydroxy acids may be derived from linolenic acid, should prove most interesting subjects for study.

Acknowledgments

The author wishes to take this opportunity to thank Dr. W. Lash Miller, Professor Emeritus of Physical Chemistry, University of Toronto, and Dr. F. B. Kenrick, Professor of Chemistry, University of Toronto, for their encouragement and advice during the course of the work; to acknowledge the technical assistance of Mr. C. W. Cosgrey in obtaining some of the data reported in this paper; and to thank Lever Brothers Limited, Toronto, for their kindness in supplying the sunflower seed oil used in the experiments.

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THE KINETICS OF THE DECOMPOSITION REACTIONS OF THE LOWER PARAFFINS

I. *n*-BUTANE[1]

BY E. W. R. STEACIE[2] AND I. E. PUDDINGTON[3]

Abstract

The kinetics of the thermal decomposition of *n*-butane has been investigated at pressures from 5 to 60 cm. and temperatures from 513 to 572° C. The initial first order rate constants at high pressures are given by

$$\log_{10} k = 12.71 - \frac{58700}{2.3RT} \text{ sec.}^{-1}.$$

The results are in good agreement with the work of Frey and Hepp, but differ greatly from that of Paul and Marek. The reaction rate falls off strongly with diminishing pressure; this is rather surprising for a molecule as complex as butane. The first order constants in a given run fall rapidly as the reaction progresses. The last two facts suggest that chain processes may be involved.

A large number of analyses of the products of reaction have been made at various pressures, temperatures, and stages of the reaction, the method being that of low-temperature fractional distillation. The products are virtually independent of temperature and pressure over the range investigated. The initial products, obtained by extrapolation to zero decomposition, are:—H_2, 2.9; CH_4, 33.9; C_3H_6, 33.9; C_2H_4, 15.2; C_2H_6, 14.1%. The mechanism of the reaction is discussed, and the results are compared with those of the other paraffin decompositions.

Introduction

In recent papers from this laboratory (38, 39, 42) dealing with the decomposition of the alkyl nitrites, it has been concluded that for a series of homologous compounds decomposing by identical mechanisms the activation energy should decrease only very slowly as the series is ascended. (Or, perhaps, remain constant if the compounds are sufficiently complex, as found by Coffin and his co-workers (3, 4, 25).)

From the point of view of the influence of chemical configuration on the reaction rate, the thermal decomposition reactions of the paraffin hydrocarbons offer unique and interesting possibilities. These reactions are also of interest by comparison with the mercury photosensitized decompositions (21, 24, 41, 43), and with the reactions of hydrogen atoms with the hydrocarbons (1, 15, 16, 34, 35, 40, 44).

The available information on the reactions of the lower paraffins has recently been reviewed by one of us (36). If the velocity constants of the decomposition reactions are expressed in the customary way by

$$k = Ae^{-E/RT},$$

we have the values of A and E given in Table I for the paraffins from methane to hexane.

It is obvious from the table that there is no agreement whatsoever among the results of different workers, and it therefore seemed worth while re-in-

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vestigating some of the reactions accurately, with special emphasis on the determination of the temperature coefficient. In considering the results given in Table I, we would naturally expect that even if the results of different workers are widely different, those obtained in the same laboratory should be at least roughly comparable. From this point of view the wide difference between the results for normal and isobutane obtained by Paul and Marek is noteworthy, and it is a matter of considerable interest to determine whether or not this difference is fictitious. It was therefore decided to re-investigate the butane decompositions first, and the present paper deals with that of *n*-butane.

TABLE I

SUMMARY OF THE RESULTS OF DIFFERENT OBSERVERS FOR THE KINETICS OF THE PARAFFIN DECOMPOSITIONS

Paraffin	Observer	$\log_{10} A$	E, Kcal.
CH_4	Kassel (20)	12.00	79.4
C_2H_6	Marek and McCluer (22)	15.12	73.2
	recalculated (26)	16.06	77.7
	Sachsse (32)	14.1	69.8
C_3H_8	Marek and McCluer (22)	13.44	62.1
	Paul and Marek (26)	16.60	74.9
n-C_4H_{10}	Frey and Hepp (14)	13.53	61.4
	Paul and Marek (26)	17.05	73.9
iso-C_4H_{10}	Paul and Marek (26)	14.89	66.0
n-C_5H_{12}	Frey and Hepp (14)	13.4	61.2
iso-C_5H_{12}	Frey and Hepp (14)	12.93	58.6
n-C_6H_{14}	Frey and Hepp (14)	12.43	55.5
	Dintzes *et al.* (8, 9)	14.58	64.5

The first investigations of this reaction were those of Pease (27) and of Pease and Durgan (28). It was shown that the reaction was homogeneous, the products being almost entirely as represented by the three equations

$$(1)\quad C_4H_{10} = C_4H_8 + H_2$$
$$(2)\quad C_4H_{10} = C_3H_6 + CH_4$$
$$(3)\quad C_4H_{10} = C_2H_4 + C_2H_6\ .$$

The rate of the reaction was only roughly measured.

Hurd and Spence (18) investigated the products of the reaction only, and concluded that Reactions (2) and (3) were the main processes. Cambron (2) suggested that the reaction

$$C_4H_{10} = 2C_2H_4 + H_2$$

also occurs at high temperatures.

Reference has already been made to the kinetic results of Frey and Hepp. The main trouble with their work from a kinetic standpoint lies in the fact

that they worked at two temperatures only, and hence their value of the temperature coefficient is not as reliable as it might otherwise be. Also, they did not study the effect of varying pressure on the rate to any great extent, and their results are not detailed enough to enable any decision to be made regarding the falling-off in rate at low pressures. Frey and Hepp made very thorough analyses of the products of the reaction by low-temperature fractional distillation. A typical analysis at 575° C. and 74.5 cm. pressure after 10% decomposition was: H_2, 5.0; CH_4, 32.1; C_2H_4, 16.3; C_2H_6, 13.2; C_3H_6, 31.1; C_3H_8, 2.2%.

Marek and Neuhaus (23) made analyses at various stages of the reaction, and concluded that the initial products were:—

	CH_4	C_3H_6	C_2H_6	C_2H_4	H_2	C_4H_8	C_3H_8
At 600° C.	24.3	24.3	17.3	17.3	8.0	8.0	0.0
At 650° C.	24.0	24.0	18.4	19.4	6.2	6.2	0.5(?)

Their values for hydrogen and butylene are thus considerably higher than those of Frey and Hepp and of Hurd and Spence.

The kinetic results of Paul and Marek have been summarized in Table I. Their work was done by a flow method, as was that of Frey and Hepp. One source of uncertainty in their work was the temperature of the reaction vessel. They used a preheater to prevent excessive cooling of the reaction vessel by the flowing gases. This was at too high a temperature, however, and in some cases 20% of the reaction occurred in the preheater. They correct for this, but on account of the fact that their experiments are thus made with partially decomposed butane it is impossible to get initial rates from their work. Their work, also, yields no information concerning the falling-off in rate at low pressures.

Some experiments on the rate of the reaction were also made by Witham (45), who also used a flow method. His rates vary so much with contact time, that little information can be obtained from them.

Experimental

In the present investigation the static method was used, so as to enable accurate temperature control, and to permit the investigation of the effect of pressure on the rate of reaction. A comparatively large reaction vessel was used, so that sufficient products were available to permit accurate analysis, and a large number of analyses were made. In this way it was possible to combine the advantages of the static and flow methods.

The apparatus is shown diagrammatically in Fig. 1. The reaction vessel was a transparent quartz flask of about 750 cc. capacity, and was connected through a graded seal to a capillary mercury manometer, and through a stopcock to a storage bulb, pumps, McLeod gauge, etc. The manometer was wound with

nichrome wire and heated electrically to a temperature of 105° C. to prevent condensation of the decomposition products. The reaction vessel was heated in an electric furnace, the temperature of which could be controlled manually to within ± 1°. The maximum temperature gradient along the furnace was less than 1.5°. The temperature was measured by means of a chromel-alumel thermocouple in conjunction with a potentiometer. The thermocouple was standardized at 0° C. and at the boiling point of sulphur.

An expansion bulb of two litres capacity connected in series with a trap was used to collect samples for analysis. The sample was obtained, after the reaction had proceeded to the desired extent, by opening a stopcock connecting the reaction vessel with the expansion chamber for 10 sec. By cooling the trap with liquid air the pressure in the expansion chamber was kept low and most of the gas in the reaction vessel could be removed in a single expansion. There was no danger of fractionating the sample by this method, since the expansion occurred rapidly through narrow tubing. Where necessary, several runs were made under identical conditions and the products combined to give a sample large enough for accurate analysis (about 600 cc.).

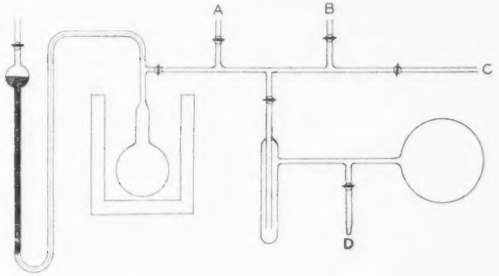

FIG. 1. *Apparatus. A, storage bulb; B, purification apparatus; C, pump; D, Toepler pump.*

The sample was transferred by means of a Toepler pump to a portable mercury gas-holder, and was then analyzed by low-temperature fractional distillation in an apparatus of the Podbielniak type. On samples of 600 cc. of gas an accuracy of about 0.2 to 0.3% could be obtained.

Prior to making a run the apparatus was evacuated to a pressure of 10^{-4} mm. Differences in ultimate pressure and in time of evacuation had no noticeable effect on the reaction rate.

C.p. butane, obtained in cylinders from the Ohio Chemical and Mfg. Co., was used. It was stated by the manufacturers to be at least 99% *n*-butane. The cylinder gas was fractionally distilled twice, the middle portion being retained each time. It was stored as a gas in a 10-litre flask connected to the apparatus.

The reaction was followed by observing the rate of change of pressure. Rates were measured at temperatures from 513° to 572° C., and at initial pressures from 5 to 60 cm. The products were examined over the same

temperature range at various initial pressures, and at various stages of the reaction, so as to permit an accurate interpretation of the results obtained by observing the pressure change. The "initial products" were found by extrapolating to zero conversion in the usual way. The time for a 12.5, 25, or 50% pressure increase was used as a measure of the rate of reaction.

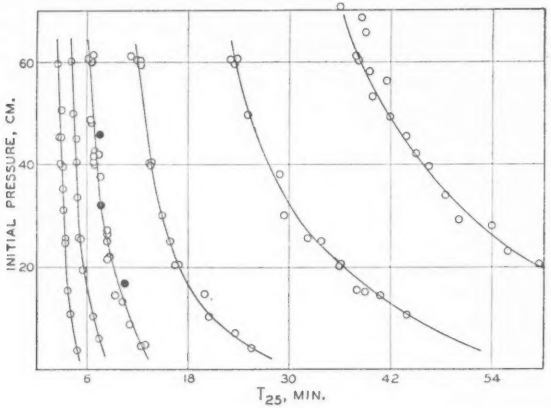

FIG. 2. *Effect of pressure and temperature on the rate of reaction. The curves from left to right represent respectively 572°, 562°, 552°, 538°, 522°, 513° C. Black circles represent results of experiments made in a packed reaction vessel.*

Results

The Rate of the Reaction

The rates of the first few experiments made in the apparatus were somewhat erratic, but after about 10 runs the rate became completely reproducible. The results of the early runs were discarded. On removing the reaction vessel at the end of the investigation it was found to be covered with a thin

TABLE II

DATA FOR A TYPICAL EXPERIMENT AT 552° C.

Initial pressure = 24.80 cm.

Time, min.	ΔP, cm.	k, sec.$^{-1}$	Time, min.	ΔP, cm.	k, sec.$^{-1}$
0	–	–	40	15.34	4.03×10^{-4}
1	1.10	7.48×10^{-4}	50	17.40	4.05
2	2.01	7.04	60	18.87	3.96
4	3.45	6.23	70	19.70	3.77
6	4.50	5.54	80	20.70	3.75
8	5.45	5.18	90	21.70	3.84
10	6.47	5.04	100	22.38	3.84
14	8.10	4.72	130	23.82	4.12
18	9.53	4.51	170	24.85	–
22	10.76	4.30	290	26.01	–
26	11.90	4.19	410	26.40	–
30	13.00	4.14	530	26.48	–

coherent layer of carbon. During the investigation a small quantity of tar-like polymer distilled from the reaction vessel into the connecting tubing. The quantity of such material formed, however, was insufficient to enable its identification. In any case, the amount of tar formed per run was too small to make any measurable difference in the gas analyses or in the pressure readings.

Several runs were carried to completion, the time required being about 14 hr. at 552° C. The pressure increase at completion was between 107 and 109%. As analysis showed that an increase in pressure of 25% corresponded exactly to 25% decomposition, it appears that secondary reactions account for the slight increase in pressure over the theoretical 100%.

TABLE III

THE VARIATION OF REACTION RATE WITH PRESSURE AND TEMPERATURE

Initial pressure, cm.	T_{25}, min.	Initial pressure, cm.	T_{25}, min.	Initial pressure, cm.	T_{25}, min.
Temperature, 515° C.					
10.80	75.0	38.90	46.2	58.50	39.5
15.10	64.5	39.80	46.5	60.10	38.1
20.15	59.5	42.16	45.0	61.20	38.0
22.30	56.0	45.40	43.2	65.45	39.0
27.90	54.0	49.30	42.0	68.80	38.7
29.30	50.4	53.35	39.8	70.60	36.0
34.20	48.5	56.50	41.7		
Temperature, 522° C.					
5.75	54.0	20.15	36.0	38.40	28.2
10.70	44.0	20.40	36.0	49.40	25.2
14.75	41.0	24.95	34.2	59.50	23.6
15.20	39.0	25.38	32.2	60.40	23.2
15.45	38.0	30.20	29.5	60.60	23.9
Temperature, 538° C.					
4.25	25.5	20.60	16.5	40.70	13.5
7.08	23.7	25.00	16.0	59.50	12.5
10.31	20.5	29.95	15.0	60.20	12.0
14.80	19.0	40.00	13.6	60.20	12.5
20.25	16.8	40.10	13.6	61.20	11.2
Temperature, 562° C.					
6.00	7.5	25.60	5.3	45.20	4.7
10.20	6.7	30.30	5.1	49.50	4.5
19.45	5.5	33.70	4.7	60.10	4.2
25.45	5.6	40.60	4.6		
Temperature, 572° C.					
4.65	4.7	31.10	3.4	45.40	3.0
10.90	4.2	35.00	3.1	45.40	2.7
15.40	3.8	39.50	3.1	50.20	3.0
25.38	3.6	39.80	2.9	59.50	2.5
25.20	3.5				

TABLE III—*Concluded*

THE VARIATION OF REACTION RATE WITH PRESSURE AND TEMPERATURE

Initial pressure, cm.	T_{25}, min.	T_{50}, min.	Initial pressure, cm.	T_{25}, min.	T_{50}, min.
Temperature, 552° C.					
4.15	12.4	40.0	40.20	7.1	21.0
4.90	13.0	39.0	40.60	6.8	20.2
8.90	11.0	33.2	41.10	7.0	21.0
13.60	10.0	29.3	41.60	7.2	21.6
21.75	8.8	25.5	42.50	7.0	21.1
22.20	8.6	26.0	47.90	6.6	19.7
25.10	8.3	24.6	48.60	6.4	19.3
26.60	8.4	26.0	59.80	6.5	19.2
27.00	8.5	25.5	60.00	6.4	17.7
32.40	7.7	23.2	61.30	6.7	18.3
37.30	7.7	22.2			
Temperature, 552° C.—Packed reaction vessel					
14.88	10.0	28.5	45.65	7.7	20.0
30.25	7.8	33.3			

Data for a typical run at 552° C. are given in Table II. The unimolecular constants in the table are calculated on the assumption that 100% pressure increase corresponds to completion. For the early stages of the reaction it would make little difference if the constants were calculated on the assumption of 108% pressure increase at completion. Justification for the use of the pressure change as a measure of the extent to which the reaction has progressed will be given in a later section.

Table III shows the effect of temperature and of initial pressure on the rate of reaction. In the table T_{25} denotes the time for a 25% increase in pressure, and T_{50} that for a 50% increase in pressure. It will be shown later that these correspond to 24.9 and 46.3% decomposition respectively.

It will be seen from the data of Table III that the rate, as inferred from T_{25} or T_{50}, falls off with diminishing pressure. In order to get high-pressure rates, $T_{12.5}$, T_{25}, or T_{50} was plotted against the reciprocal of the pressure and extrapolated to infinite pressure, as shown in Fig. 3. The values of the infinite pressure rate constants given in Table IV were thus obtained.

In Table IV in addition to the values of the high-pressure rate constants the limiting ratios of T_{25} to $T_{12.5}$, and of T_{50} to T_{25} have been tabulated. It will be shown later that $T_{12.5}$, T_{25}, and T_{50} correspond to 12.5, 24.9, and 46.3% reaction respectively. Whence it follows that the theoretical values of the two ratios are both 2.16 for a first order reaction. These are much lower than the experimental values.

The fact that the theoretical values of these ratios do not hold is in accord with the results of Table II, which show that the first order constants in an individual run fall off strongly as the reaction progresses. Similar behavior

has been noted by Dintzes and co-workers (5, 6, 7) in the decompositions of ethane and propane, and this is undoubtedly due to the existence of secondary changes of some kind.

TABLE IV

LIMITING HIGH PRESSURE RATE CONSTANTS

Temperature, °C.	$T_{12.5}$, sec.	T_{25}, sec.	T_{50}, sec.	$\frac{T_{25}}{T_{12.5}}$	$\frac{T_{50}}{T_{25}}$	$k_\infty \times 10^4$, sec.$^{-1}$, calculated from T_{25}
513	573	1788	–	3.12	–	1.61
522	339	1092	–	3.22	–	2.64
538	198	600	–	3.30	–	4.69
552	101	342	840	3.39	2.46	8.41
562	69.6	216	504	3.11	2.33	13.3
572	–	120	297	–	2.47	24.0

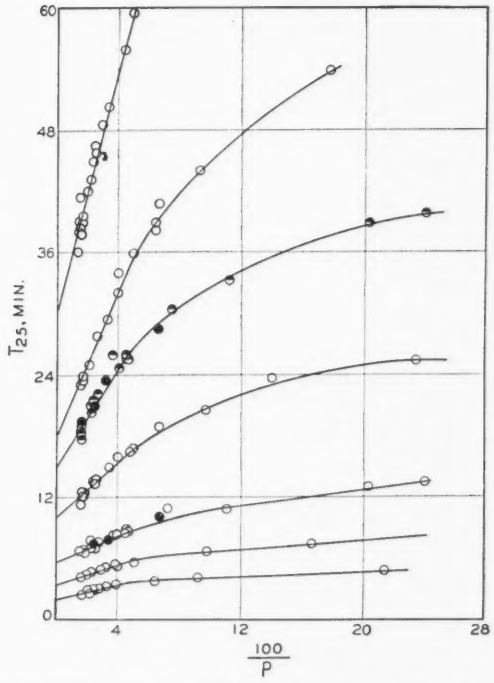

FIG. 3. *Extrapolation of rates to infinite pressure. From top to bottom the curves represent successively: T_{25} at 513° C., open circles; T_{25} at 522° C., open circles; T_{50} at 552° C., half-black circles; T_{25} at 538° C., open circles; T_{25} at 552° C., open circles; T_{25} at 562° C., open circles; T_{25} at 572° C., open circles. Full black circles represent results of experiments made in a packed reaction vessel.*

This divergence of the constants from the theoretical behavior raises the question of the validity of using $T_{12\cdot5}$ or T_{25} as a measure of the rate of reaction, since the calculated velocity constant will depend on the extent to which the reaction has progressed. From the point of view of the determination of the activation energy of the reaction, the important point is whether or not the reaction rate curves have identical forms at different temperatures. If they do, then the relative values of the velocity constants at different temperatures inferred from the time to any given fractional amount of reaction will be in the same ratio, and the calculated value of the activation energy will not be affected by the drift of the first order rate constants. The simplest way of checking the form of the reaction rate curves is to compare values of the ratios $T_{25}/T_{12\cdot5}$ and T_{50}/T_{25} at various temperatures and pressures. If these ratios remain constant there is no doubt that the curves are affine.

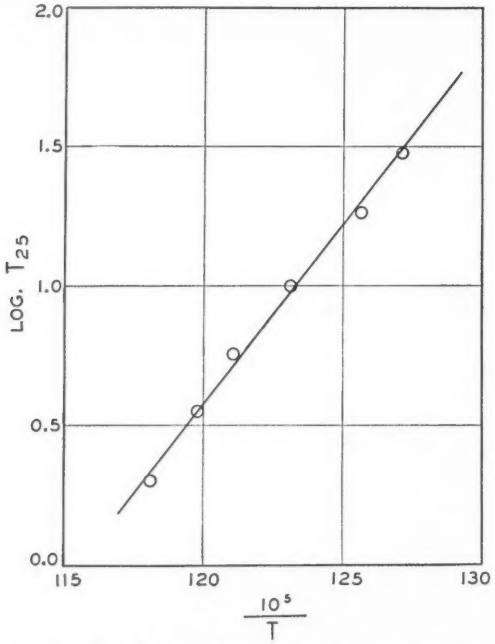

FIG. 4. *The effect of temperature on the rate of reaction.*

Table V gives data of this sort for typical runs. It is obvious from Tables IV and V that there is no significant change in the values of the ratios with changing temperature at any given pressure, including the extrapolated values at infinite pressure. We may therefore use the values given in Table IV to calculate the activation energy of the reaction, and this has been done graphically in Fig. 4. From the slope of the line a value of 58,700 cal. per mole is obtained for the energy of activation. From this value we obtain for

TABLE V

VALUES OF T_{50}/T_{25} AND $T_{25}/T_{12.5}$ AT VARIOUS TEMPERATURES AND PRESSURES

Temperature, °C.	$T_{12.5}$, sec.	T_{25}, sec.	T_{50}, sec.	$\frac{T_{25}}{T_{12.5}}$	$\frac{T_{50}}{T_{25}}$
Initial pressure, 50 cm.					
513	894	2544	–	2.84	–
522	534	1512	–	2.83	–
538	269	762	–	2.83	–
552	145	420	1182	2.90	2.82
562	94.8	270	738	2.85	2.73
572	–	169	486	–	2.87
Initial pressure, 33.3 cm.					
513	1056	2922	–	2.78	–
522	630	1716	–	2.72	–
538	305	840	–	2.75	–
552	167	456	1356	2.73	2.97
562	107	295	858	2.76	2.91
572	–	192	582	–	3.02
Initial pressure, 25 cm.					
513	–	–	–	–	–
522	729	1920	–	2.63	–
538	339	924	–	2.72	–
552	189	493	1524	2.61	3.08
562	117	324	972	2.76	3.01
572	–	216	675	–	3.13

the high pressure rate of reaction as a function of temperature the equation

$$\log_{10} k = 12.54 - \frac{58700}{2.3RT} \text{ sec.}^{-1}.$$

High pressure rates obtained from values of T_{50} or $T_{12.5}$ give identical values of the activation energy, thereby justifying the use of times to fractional amounts of reaction as a measure of the rate.

As pointed out above, the velocity constants fall off in an individual run as the reaction progresses. The true rate of reaction is, of course, the initial rate and not that obtained at a later stage. Extrapolation of the results to obtain initial rates is not easy, but the indications from a large number of runs are that the initial velocity constants are almost exactly 50% higher than those calculated at 25% completion. Hence for the *initial* high pressure rate we have

$$\log_{10} k = 12.71 - \frac{58700}{2.3RT} \text{ sec.}^{-1}.$$

The full circles in Fig. 3 represent runs made in a reaction bulb packed with broken silica tubing, the surface-volume ratio of which was approximately 15 times greater than that of the empty vessel. These experiments prove that the reaction is not appreciably heterogeneous.

The Products of the Reaction

Analyses of the products of the reaction were made by low-temperature fractional distillation on samples removed at $T_{12\cdot5}$, T_{25}, and T_{50} at initial pressures from 20 to 60 cm., over the whole temperature range. Analyses from runs at lower initial pressures were not feasible on account of the small amount of products available. The results of the analyses are given in Tables VI and VII.

TABLE VI

THE PRODUCTS OF THE REACTION AT VARIOUS TEMPERATURES AND AN INITIAL PRESSURE OF 60 CM.

Temperature, °C.	513	522	538	552	562	572	Mean
			Products, mole per cent				
Sample withdrawn at T_{50}							
H_2	2.0	2.8	1.5	1.8	0.5	1.7	1.7
CH_4	39.1	38.2	38.7	40.0	40.5	38.9	39.2
C_2H_4	15.1	15.9	15.8	16.0	15.8	16.2	15.8
C_2H_6	14.1	14.2	14.2	12.6	13.5	12.6	13.5
C_3H_6	29.8	28.8	29.5	29.6	29.7	30.2	29.6
% C_4H_{10} decomposed	45.0	45.2	45.4	50.2	45.7	46.0	46.3
Sample withdrawn at T_{25}							
H_2	0.0	2.0	1.2	0.5	2.0	—	1.1
CH_4	36.0	36.2	36.0	39.0	35.5	—	36.5
C_2H_4	16.1	15.8	15.9	15.8	16.3	—	16.0
C_2H_6	13.9	12.0	13.3	12.6	13.7	—	13.1
C_3H_6	33.9	34.0	33.5	32.2	32.9	—	33.3
% C_4H_{10} decomposed	23.1	24.6	24.7	26.2	25.8	—	24.9
Sample withdrawn at $T_{12\cdot5}$							
H_2	2.1	1.5	0.8	2.5	—	—	1.7
CH_4	33.5	36.0	37.4	34.7	—	—	35.4
C_2H_4	15.0	14.9	15.4	15.7	—	—	15.2
C_2H_6	14.7	14.6	13.8	13.5	—	—	14.2
C_3H_6	34.7	33.0	32.5	33.6	—	—	33.5
%C_4H_{10} decomposed	11.4	12.7	13.5	12.7	—	—	12.6

It follows from Table VI that T_{50}, T_{25}, and $T_{12\cdot5}$, as measured by the pressure change, really correspond to 46.5, 24.9, and 12.6% decomposition respectively.

In the analyses reported above, hydrogen and methane were distilled off together, and this fraction was analyzed for the separate constituents by combustion. Butene has frequently been reported as a product of the decomposition. With small samples it is difficult to detect since its boiling point is close to that of butane, which is of course present in large quantity. In a number of cases attempts were made to determine butene by analyzing the butane-butene fraction from a distillation for unsaturates, by use of

fuming sulphuric acid as the absorbent in a Burrell gas analysis apparatus. The method is complicated to some extent by the fact that some butane is absorbed by the reagent, and blank runs had to be made to correct for this. The results indicated that if any butene were present its amount was not more than 1%, and even this small amount may have been partly due to propylene which had not been perfectly cut from butane. It may therefore be concluded that no significant amount of butene is present, and it has not been reported in the tables.

TABLE VII

THE PRODUCTS OF THE REACTION AT VARIOUS INITIAL PRESSURES

Initial pressure, cm.	60	40	20
	Products, mole per cent		
552° C. Sample withdrawn at T_{50}			
H_2	1.8	1.5	2.4
CH_4	40.0	38.6	39.1
C_2H_4	16.0	17.8	17.0
C_2H_6	12.6	12.8	12.8
C_3H_6	29.6	29.2	28.8
% C_4H_{10} decomposed	50.2	46.4	47.0
552° C. Sample withdrawn at T_{25}			
H_2	0.5	2.4	0.9
CH_4	39.0	36.0	36.5
C_2H_4	15.8	18.4	16.4
C_2H_6	12.6	11.7	13.8
C_3H_6	32.2	31.6	32.2
% C_4H_{10} decomposed	26.2	26.3	24.1
552° C. Sample withdrawn at $T_{12.5}$			
H_2	2.5	1.4	—
CH_4	34.7	36.6	—
C_2H_4	15.7	15.0	—
C_2H_6	13.5	13.7	—
C_3H_6	33.6	33.4	—
% C_4H_{10} decomposed	12.7	13.6	—
538° C. Sample withdrawn at T_{25}			
H_2	1.2	0.3	—
CH_4	36.0	36.5	—
C_2H_4	15.9	16.1	—
C_2H_6	13.3	13.3	—
C_3H_6	33.5	33.2	—
% C_4H_{10} decomposed	24.7	24.5	—

It follows from Table VII that there is no noticeable variation of products with changes in initial pressure over the range from 20 to 60 cm. Owing to the difficulty in obtaining a sample sufficiently large for analysis, no attempt was made to determine the products of runs made at lower initial pressures.

Table VI shows that over the range used there is little variation in the products of reaction with temperature. In view of this, mean values of products at T_{50}, T_{25}, and $T_{12.5}$ have been used in extrapolating to zero conversion to get the initial products. Fig. 5 shows the result of this extrapolation. If we assume the difference between the percentages of methane and propylene to be due to hydrogen, the following percentages are obtained for the initial products: H_2, 2.9; CH_4, 33.9; C_3H_6, 33.9; C_2H_4, 15.2; C_2H_6, 14.1. The fact that the quantity of ethylene is greater than that of ethane may be due to the occurrence to a small extent of the reaction postulated by Cambron

$$C_4H_{10} = 2C_2H_4 + H_2 ,$$

or perhaps more likely to a small amount of secondary dehydrogenation of ethane.

$$C_2H_6 = C_2H_4 + H_2 .$$

The hydrogen-carbon ratio calculated from the mean values of the products in Table VI has the values 2.59, 2.52, and 2.52 at T_{50}, T_{25}, and $T_{12.5}$ respectively. This is in satisfactory agreement with the theoretical value of 2.50, and indicates that no appreciable quantity of tar or higher polymers can have been formed during the early stages of the reaction. The hydrogen-carbon ratio for the initial products, as obtained by extrapolation, is 2.52.

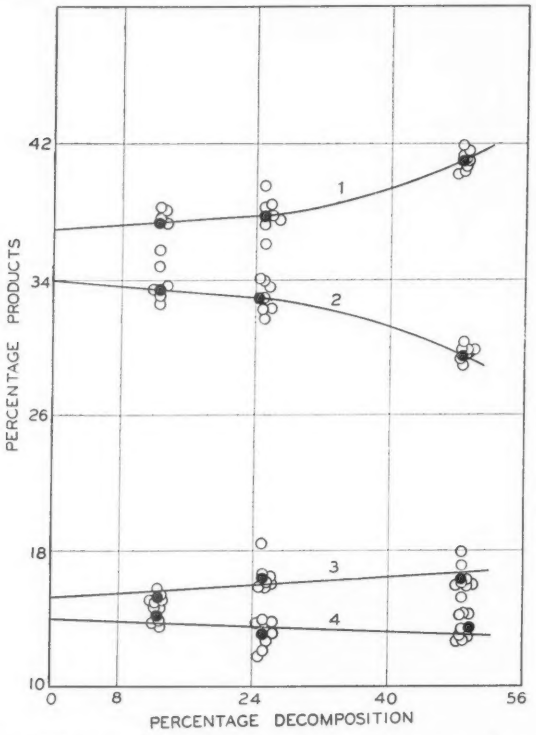

FIG. 5. *Extrapolation to determine initial products of the reaction. Curve 1 represents* $CH_4 + H_2$; *Curve 2,* C_3H_6; *Curve 3,* C_2H_4; *Curve 4,* C_2H_6. *Open circles represent actual analyses; black circles represent mean values.*

Discussion

The Products of the Reaction

The products obtained by previous workers have been discussed in the Introduction. The products reported above show excellent general agreement with the work of Hurd and Spence (18) and of Frey and Hepp (14). The agreement with the work of Marek and Neuhaus (23) is not good. Thus for the ratio $(CH_4 + C_3H_6)/(C_2H_4 + C_2H_6)$ our work indicates a value of about

2.3 for the initial products at temperatures up to 572° C., in agreement with Frey and Hepp's value at 575° C. and 10% decomposition of 2.15. Marek and Neuhaus from the initial products at 600° C., however, obtain a value of 1.4, and the discrepancy cannot be attributed to the difference in temperature, since all observers agree that temperature has little effect on the products in this range.

Our results are in qualitative agreement with Rice's suggested free radical mechanism (31), inasmuch as the only important products are CH_4, C_3H_6, C_2H_4, and C_2H_6. However, the Rice mechanism indicates a value for the above ratio of 1.33, which is very different from that found. Actually, however, this ratio, on the Rice mechanism, is entirely dependent on purely arbitrary assumptions regarding the relative reactivity of primary and secondary hydrogen atoms, and it would not be difficult to devise a free radical mechanism which would agree with the products found.

The Rate of the Reaction

If we compare the values of E, A, and of the velocity constant at, say, 575° C. with those of other workers, we obtain, using the initial rates from our work,

	E, Kcal.	$\log_{10} A$	k_{575}, sec.$^{-1}$
Frey and Hepp	61.4	13.53	4.8×10^{-3}
Paul and Marek	73.9	17.05	9.8×10^{-3}
Steacie and Puddington	58.7	12.71	3.7×10^{-3}

In view of the limited number of experiments made by Frey and Hepp, the agreement of their work with ours is entirely satisfactory. There is, however, a very large discrepancy between these results and those of Paul and Marek, amounting to 15 Kcal. in E and over 10,000 in A.

One cause of uncertainty in previous work has been the use of k's determined at atmospheric pressure in determining E, instead of the use of high pressure k's. The falling-off in rate with pressure varies with temperature, and hence activation energies determined from observed velocities at lower pressures will be too high. Thus from our results we get

True E	58.7 Kcal.
E from P = 76 cm.	66.2
E from P = 50 cm.	66.4
E from P = 33 cm.	= 66.7
E from P = 25 cm.	= 67.0.

In other words the activation energy determined from experiments at atmospheric pressure is about 7.5 Kcal. too high. The results of Paul and Marek and of Frey and Hepp were obtained at atmospheric pressure, and should therefore be too high by approximately the same amount. If we arbitrarily correct them, we obtain

Frey and Hepp	54.5 Kcal.
Paul and Marek	67.0
Present work	58.7.

This gives somewhat better agreement, although the results of Paul and Marek are still definitely far too high by comparison.

In Table I we have given a summary of kinetic data for the paraffin decompositions. In view of the present work it appears probable that the results of Marek and his co-workers may be too high in all cases, and that those of Frey and Hepp are to be preferred when available. On this basis it may be tentatively suggested that the best values of the activation energies of the paraffin decompositions are not far from: CH_4, 79; C_2H_6, 70; C_3H_8, 62; n-C_4H_{10}, 59; n-C_5H_{12}, 56; n-C_6H_{14}, 55 Kcal. In other words, it is probable that there is a steady decrease in the activation energy as we ascend the series, leading to a limiting value for the higher members of about 55 Kcal.

As pointed out above, the products of the reaction do not vary significantly within the temperature range investigated. The activation energies of the separate decompositions

$$C_4H_{10} = CH_4 + C_3H_6 \qquad (1)$$

and

$$C_4H_{10} = C_2H_4 + C_2H_6 \qquad (2)$$

therefore appear to be identical and equal to the observed value for the over-all reaction of 58.7 Kcal. We may also apportion the velocity constants between the separate reactions and write for the initial high pressure rates:

$$\log_{10} k_1 = 12.55 - \frac{58700}{2.3RT} \text{ sec.}^{-1}$$

$$\log_{10} k_2 = 12.19 - \frac{58700}{2.3RT} \text{ sec.}^{-1}$$

Free Radicals in the Butane Decomposition

It has been shown by Rice, Johnston, and Evering (30) that free radicals can be detected in the high temperature decomposition of n-butane, and Rice and Johnston (29) have found the activation energy of the free radical split to be 65.4 Kcal. Rice has suggested (31) that the ordinary thermal decomposition at lower temperatures occurs by a free radical chain mechanism. As we have shown above, the Rice scheme leads to the correct products of the reaction, although the relative amounts of the various products are not in good agreement with his predictions.

The kinetic consequences of such free radical chain mechanisms have been found to be in general disagreement with experiment for ethane and propane (see (36) for a full discussion). In the case of butane, however, there is a great deal of evidence to show that radicals are involved in the thermal decomposition, at least to some extent. Thus by various methods Heckert and Mack (17), Frey (13), Echols and Pease (10, 11), Sickman and Rice (33), and Steacie and Folkins (37) have shown that chain decomposition of n-butane can be initiated by radicals, or that chains occur in the ordinary thermal decomposition to some extent. The present investigation has shown that the activation energy of the decomposition is 58.7 Kcal., which is very little

below Rice and Johnston's estimate of 65.4 Kcal. for the split into radicals. In other words, if we assume a chain mechanism, the over-all activation energy is only slightly lower than the activation energy for the primary step, and it appears therefore that in this case it is possible that the primary step is a split into radicals, followed by the setting up of quite short chains. Similar considerations would apply to all the higher hydrocarbons, since it seems probable that the thermal and free radical activation energies are converging to the same value for the higher paraffins. However, it remains for further work to decide the question.

The Effect of Pressure on the Rate of Reaction

It will be seen from the data of Table III and Figs. 2 and 3 that the rate of reaction falls off with diminishing pressure at quite high pressures. The Kassel equation for the effect of pressure on the rate is (19)

$$k/k_\infty = \left(1 - e^{-\frac{h\nu}{kT}}\right)^s \sum_{j=m}^{\infty} \frac{\binom{j - m + s - 1}{j - m} e^{-(j-m)h\nu/kT}}{1 + \frac{A(j - m + s - 1)!\, j!}{aN(j - m)!\,(s - 1)!}}$$

where N is the number of molecules per cubic centimetre, a is a collision factor which involves the molecular diameter σ, s is the number of oscillators in the molecule ($(3n - 6)$, where n is the number of atoms) less the number of C—H bonds, since the C—H valence vibrations are not likely to be thermally excited at the temperature in question, j is the number of vibrational quanta possessed by the molecule, m is the number of quanta which must be localized in the pertinent bond in order that reaction may occur, and ν is the frequency of the oscillators, all of which are for simplicity assumed to be identical. If we apply the equation, putting

$$\begin{aligned} s &= 26 \\ \sigma &= 4 \times 10^{-8} \text{ cm.} \\ N_0 mh\nu &= 58.7 \text{ Kcal. } (N_0 = \text{Avogadro's number}), \end{aligned}$$

we find that for all values of ν from 200 to 3000 cm.$^{-1}$ no falling off in rate is predicted until pressures below 1 mm. are reached. If we assume that half the molecule is "frozen" from the point of view of the reaction, and put

$$\begin{aligned} s &= 6 \\ \sigma &= 4 \times 10^{-8} \text{ cm.} \\ m &= 18 \\ \nu &= 1141 \text{ cm.}^{-1}, \end{aligned}$$

we get perfect agreement with experiment, as shown by Fig. 6, in which the line represents the theoretical curve and the circles the experimental points at 552° C. Such a freezing-out of part of the molecule is, perhaps, plausible in the case of a molecule such as diethyl ether where there is an atom in the centre which differs from those at the ends, and which might make energy transfer difficult owing to the difference in the frequency of the valence

vibrations. It seems, however, very unlikely that such an explanation could be valid in the case of a molecule like butane which contains nothing but C—H and C—C bonds. It is therefore much more likely that this surprisingly great falling-off in rate for a molecule as complex as butane is to be ascribed to chain processes. It should also be pointed out that the variation in the drift of the unimolecular constants with pressure, as shown by Table V, although small, may be a complicating factor. It is hoped that further work will throw some light on this point.

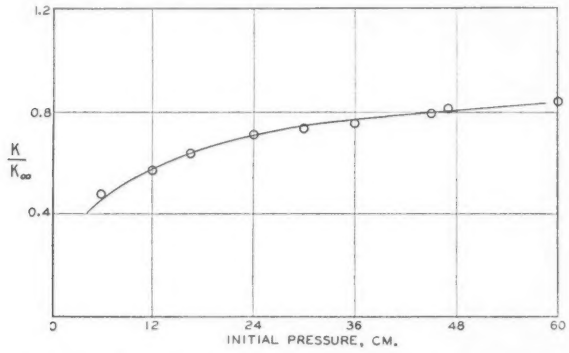

FIG. 6. *The falling-off in rate with diminishing pressure. Circles represent typical experimental results at 552° C. The curve is theoretical, using,* $s = 6$, $\sigma = 4 \times 10^{-8}$ *cm.*, $m = 18$, $\nu = 1141$ *cm.*$^{-1}$.

An investigation of the decomposition of isobutane and of normal pentane is in progress. It is planned to extend the work in the future to propane and other hydrocarbons, and it is hoped that eventually sufficient accurate data will be available to enable a more extended discussion of the influence of chemical configuration on the reaction rate.

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